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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIV SEPTEMBER 1959 No. 9

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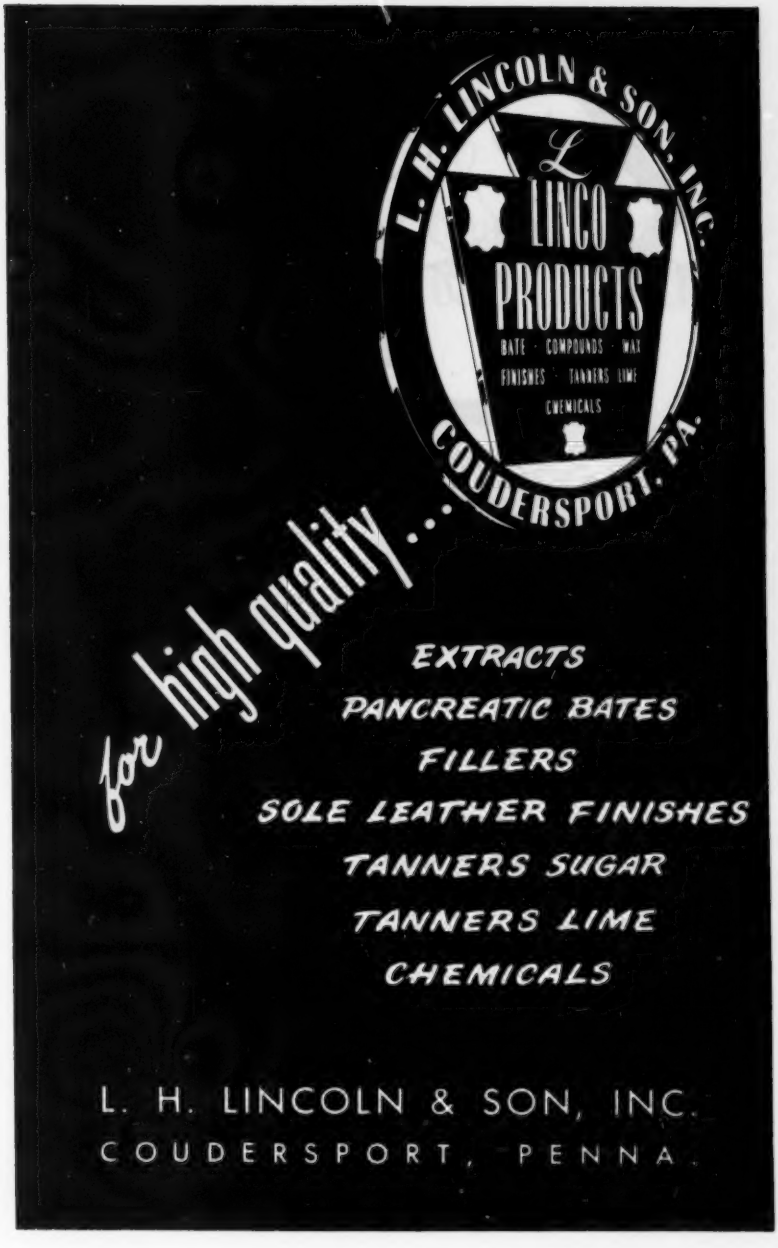
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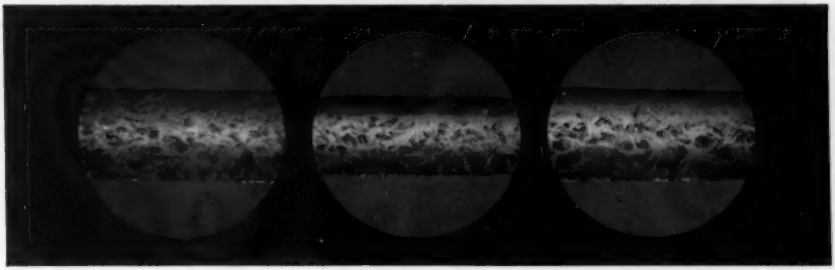

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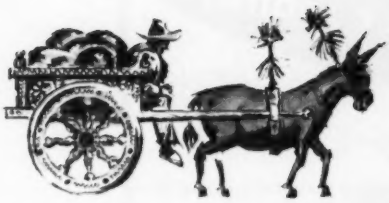

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General correspondence concerning the *Journal* should be mailed to the Managing Editor.
Subscriptions—$12 per year for members; $15 for nonmembers.

TANNING WITH GLUTARALDEHYDE

I. RATE STUDIES*

M. L. Fein, E. H. Harris, Jr., J. Naghski, and E. M. Filachione†

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ABSTRACT

In this study the tanning properties of glutaraldehyde were evaluated under various conditions and compared with results obtained using other aldehydes under the same conditions. Whole sheepskins (Syrian) were used in this investigation. Measuring the disappearance of glutaraldehyde from the tanning liquor provided a sound basis for evaluation of the over-all rate of tanning and fixation. Tanning was effected over a wide range of conditions. The rate of tanning and uptake of glutaraldehyde increased rapidly with increase of pH and concentration. Maximum shrink temperature also was attained rapidly and, in the higher pH ranges, was reached in about one hour. Tanning was effected with as little as 1.5% (based on the drained pickled weight) of active aldehyde. Under certain conditions complete exhaustion of glutaraldehyde could be obtained from the tanning liquors. This behavior is in marked contrast to that observed in the case of formaldehyde or glyoxal. Under comparable conditions of tanning with these three aldehydes the rate of tanning increased in the order: glyoxal, formaldehyde, and glutaraldehyde.

—×—×—

INTRODUCTION

The availability in recent years of several new aldehydes, particularly dialdehydes, has stimulated research to investigate the tanning action of these new members of this important and reactive class of organic compounds (1–3). Formaldehyde has been by far the best known aldehyde as regards tanning action. The formaldehyde-collagen reaction has been studied extensively, and considerable information concerning this reaction has been published. Its importance in leather chemistry is clearly evident from the

*Presented at the Fifty-fifth Annual Meeting of the ALCA at Mackinac Island, Michigan, June 14–17, 1959.
†Dr. E. M. Filachione is the senior author.
‡Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

many review articles appearing in the literature (4–8). Recent research in our laboratory (2) indicated that glutaraldehyde possessed versatile tanning power and appeared to be in the class with formaldehyde as regards reactivity. In view of the commercial availability of glutaraldehyde at relatively low cost, further study of its tanning action was most desirable. In this paper is reported a detailed study of the theoretical and practical aspects of the interaction between hide substance and glutaraldehyde. In these studies we chose to use an entire skin instead of hide powder or small pieces, in order more nearly to approach tannery practice and to enable a preliminary evaluation of the process, particularly in comparison with formaldehyde.

EXPERIMENTAL

Apparatus, chemicals, and skins.—The tanning experiments on one skin at a time were run in a small drum (approximately 17½″ inside diameter, 8″ wide) at a speed of 10 rpm. The drum was held at 84° to 88°F. in a thermostatically controlled enclosure. A time-clock and switch arrangement allowed the drum to turn continuously from 8:00 A.M. to 5:00 P.M. and then intermittently (½ hour on, ½ hour off) the remaining hours of a 24-hour period.

The glutaraldehyde used in these experiments was a 25% aqueous solution available commercially. The glyoxal used was a specially purified grade free of formaldehyde and ethylene glycol. The formaldehyde used in several runs was the standard N.F. (37%) grade. The various salts used in the experiments described were of standard laboratory quality. All skins were commercial, degreased, pickled Syrian sheepskins.

Tanning procedure for rate studies.—The following is an outline of a typical tanning run using glutaraldehyde (25% commercial solution). All quantities are based on the drained pickled weight of the skin (DPW).

The pickled skin was added to a solution consisting of water (100%), Na_2SO_4 (10%), or NaCl (6%) and glutaraldehyde solution (variable from 6 to 24%). The drum was rolled for ½ hour. At this time a shrinkage temperature (Ts) specimen was cut from the neck area of the skin, and a 5-ml. aliquot of the tanning liquor was removed for analysis and pH determination.

Since the water present in the wet skin dilutes the tanning solution, this short drumming in the pickled condition was necessary to equilibrate or uniformly distribute the water-soluble components in the aqueous phase of the system. Although there was some fixation of aldehyde in the pH near 2, the amount in the first half hour was slight (Fig. 1). Thus, analysis of the aliquot after this half-hour treatment of the pickled skin provided a reasonably accurate estimation of the initial aldehyde concentration.

TABLE I

EFFECT OF TANNING VARIABLES ON UPTAKE OF ALDEHYDE

Exp. No.	Tanning Solution*		Aldehyde Content of Tanning Soln., g/100 ml.					
	Aldehyde %	Buffer System	pH†	Initial‡	1 hr.	2 hr.	4 hr.	8 hr.	24 hr.
			Glutaraldehyde, 25% solution						
1	6	NaCl, Na_2SO_4**	2.4–2.6	0.82	0.72	0.70	0.62	0.50	0.37
2	10	" "	2.5–2.7	1.29	1.17	1.13	0.97	0.84	0.65
3	12	formate, NaCl	4.1	1.46	0.96	0.79	0.62	0.51	0.38
4	24	" "	3.9–4.1	2.96	2.32	2.16	2.09	1.98	1.84
5	6	acetate, NaCl	4.9–5.1	0.88	0.35	0.25	0.19	0.13	0.09
6	12	" "	5.0	1.63	0.92	0.77	0.74	0.64	0.51
7††	"	" "	4.8	1.03	0.62	0.55	0.49	0.45	0.39
8	24	" "	5.0	3.11	2.23	2.11	1.98	1.89	1.69
Blank	12	" "	4.5	1.78	1.73	—	1.75	1.71	1.73
9	6	borax, NaCl	6.1–6.5	0.85	0.12	0.08	0.06	0.05	0.05
10	"	" Na_2SO_4	6.2–6.7	0.78	0.11	0.06	0.04	0.03	0.03
11	12	" "	6.4–6.7	1.47	0.51	0.39	0.29	0.22	0.15
12	24	" "	6.1–6.5	2.86	1.82	1.62	1.56	1.37	1.25
Blank	12	" "	6.4–6.6	1.86	1.78	—	1.79	1.78	1.81
13	6	$NaHCO_3$, NaCl	7.5–8.3	0.83	0.10	0.06	0.04	0.03	0.02
14	"	" Na_2SO_4	7.9–8.4	0.87	0.06	0.03	0.02	0.02	0.01
15	12	" "	7.6–8.4	1.50	0.44	0.26	0.14	0.09	0.07
16	24	" "	7.6–8.2	2.86	1.69	1.49	1.36	1.19	0.96
Blank	12	" "	7.2–8.0	1.73	1.69	—	1.70	1.67	1.54
17	6	$NaHCO_3$+MgO,Na_2SO_4	9.4–9.8	0.75	0.02	0.02	0.02	0.01	0.01
18	12	" "	9.2–9.6	1.55	0.24	0.12	0.09	0.06	0.05
19	24	" "	9.0–9.7	2.79	1.16	0.66	0.54	0.37	0.24
Blank	12	" "	9.2–10.1	1.83	1.60	—	0.61	0.35	0.23

			Formaldehyde, 37% solution						
20	4.9	acetate, NaCl	4.7–4.8	1.11	0.74	0.74	0.74	0.74	0.73
21‡‡	"	" "	4.7–4.8	0.58	0.56	0.55	0.55	0.56	0.55
22	"	$NaHCO_3$, Na_2SO_4	7.3–8.0	1.08	0.73	0.70	0.66	0.65	0.61
23	"	$NaHCO_3$+MgO, "	9.1–9.9	1.04	0.66	0.61	0.59	0.55	0.53
Blank	"	" "	9.4–10.5	1.13	1.16	—	1.12	1.13	1.10
"	"	acetate "	4.7–4.8	1.13	1.11	—	1.11	1.16	1.15
			Glyoxal, 30% solution						
24	5.8	acetate, NaCl	4.8	0.98	1.03	1.03	1.03	1.00	0.97
25	"	$NaHCO_3$, Na_2SO_4	7.3–8.1	1.10	0.97	0.83	0.65	0.47	0.31
Blank	"	acetate, NaCl	4.5–4.7	1.13	1.15	—	1.13	—	1.12
"	"	$NaHCO_3$, Na_2SO_4	7.6–8.0	1.17	1.13	—	1.10	1.12	1.11
"	"	$NaHCO_3$+MgO, "	9.2–10.2	1.08	0.74	—	0.08	—	0.02

*Based on drained pickled weight: 100% H_2O; and where listed: NaCl, 6%; Na_2SO_4 (anhyd.), 10%; sodium formate, 5%; sodium acetate (anhyd.), 6%; borax, 7.25%, $NaHCO_3$, 5%; MgO, 3%.

†Range after addition of buffer.

‡After 1/2 hour equilibration of pickled skin.

**6% Na_2SO_4 instead of 10%.

††Differed from Expt. #6 in that 200% water and 12% NaCl were used (2:1 float).

‡‡Differed from Expt. #20 in that 200% water and 12% NaCl were used (2:1 float).

At the end of this half-hour equilibrating period the solid buffering agent was promptly added in one feed, for example, $NaHCO_3$ (5%), and the drum was started in motion again. The above sampling procedure, i.e., Ts specimen from neck area and 5-ml. aliquot of tanning solution, was repeated at intervals of 1, 2, 4, 8, and 24 hours after addition of the buffer. The Ts specimens were washed for 2 hours, and the shrinkage temperature was determined.

Variations in this tanning procedure were concerned usually with the use of several different aldehydes, concentration of aldehyde, and the pH (type of buffer) of tanning. In the experiments where other aldehydes (formaldehyde or glyoxal) were used in place of glutaraldehyde, the quantity of active aldehyde equivalent to that in 12% commercial glutaraldehyde solution (based on the drained pickled weight) was calculated. This amount was then used in these comparison experiments, so that the concentrations of aldehyde or active groups were equivalent in each case. The various tanning variables investigated and the results obtained are summarized in Table I and Figs. 1 to 10.

To determine the effect on the aldehydes of the buffer and salts at the various pH levels of these tanning experiments, several "blanks" or controls were carried out. These blank runs duplicated the tanning run corresponding to the use of 12% glutaraldehyde (based on the drained pickled weight) or its equivalent of other aldehyde, except that the skin was absent. Water and acid approximating that which would have been introduced with the stock were allowed for, and the same buffering systems as in the tanning run were used. This solution was agitated by drumming, and samples were periodically withdrawn and analyzed for aldehyde content exactly as those from the tanning counterpart. These results which show the stability (or lack of stability) of the aldehydes under the various tanning conditions are also included in Table I and the various figures.

At the end of 24 hours of tanning, the full skins from this rate-of-tanning study were thoroughly washed and prepared for conversion into finished leather as described in a later section.

Determination of aldehyde content of solutions.—*General:* The method of analysis selected was a modification (9) of the iodimetric method of Romijn (10). This method is based on measuring the amount of aldehyde fixed by sodium bisulfite. This reagent, used in excess, reacts rapidly with aldehydes to form relatively stable complexes. Excess bisulfite is destroyed with iodine, and a measured excess of iodine and alkaline buffer quantitatively oxidizes both the bisulfite and aldehyde moieties of the complex. Excess iodine is then determined by titration with standard sodium thiosulfate. A blank is run at the same time, and the difference in thiosulfate is equivalent to aldehyde-bisulfite complex. The reactions involved are as follows:

$$RCHO \cdot NaHSO_3 + 2I_2 + 3Na_2CO_3 \rightarrow RCOONa + Na_2SO_4 + 4NaI + 3CO_2 + H_2O$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ NaI$$

To test the applicability and reliability of this analytical procedure the bisulfite complexes of glutaraldehyde and glyoxal were prepared and recrystallized by the procedure recommended for glyoxal (11). Sodium bisulfite formaldehyde complex was also purified in this manner. A sulfate ash analysis indicated a purity of 98.0 to 99.6% for these complexes. Solutions containing a known amount of these complexes were prepared and analyzed by this procedure. The results are shown in Table II.

TABLE II

ANALYSIS OF STANDARDS

Bisulfite Complex	Aldehyde Concn., g/100 ml.	
	Found	Theory
Formaldehyde	0.222	0.224
Glyoxal	0.199	0.206
Glutaraldehyde	0.980	0.993
" (2:1 dilution)	0.493	0.497
" (5:1 ")	0.196	0.198
" (10:1 ")	0.098	0.099

Analysis of tanning solutions: The samples periodically withdrawn from the tanning solution were filtered into small glass-stoppered bottles. From these bottles were pipetted the one-ml. samples used in the analysis. At times, some samples required dilution before analysis. This was true whenever the analysis indicated the tanning solution to be more concentrated than about 0.10 millimoles of aldehyde/ml. for the dialdehydes and about 0.25 millimoles of aldehyde/ml. for formaldehyde. In these cases one ml. of the tanning solution was diluted to 5 ml. (in a volumetric flask), and one ml. of the diluted solution was employed. The details of the analysis procedure were as follows:

Each analysis and blank was run in duplicate, using calibrated pipets, burets, and volumetric flasks.

One ml. of filtered tanning solution was pipetted precisely into a 125-ml. Erlenmeyer flask. Then 10 ml. of distilled water were added, and this was followed by 5 ml. of approximately 0.1*N* $NaHSO_3$. A reaction time of 15 minutes was allowed, and then 10 drops of starch solution were added as indicator. Next, iodine solution (approximately 0.1*N*) was added carefully to the end point to destroy excess bisulfite. When the end point was reached, exactly 10 ml. of the same iodine was added by pipet. Then 5 ml. of Na_2CO_3(2*N*) solution were added, and the flask was covered and placed in the dark (cabinet) for 20–30 minutes. Next, 10 ml. H_2SO_4(1*N*) were added (one drop was checked on indicator paper to be sure reaction mixture was acidic), and the flask was replaced in the dark for an additional 10 minutes.

The entire contents of the flask were then carefully titrated with sodium thiosulfate (0.1000*N*) to the end point.

Simultaneously a blank was run, exactly as described above except for omission of the tanning solution. Thus, only the thiosulfate need be standardized and enters into the calculations as follows:

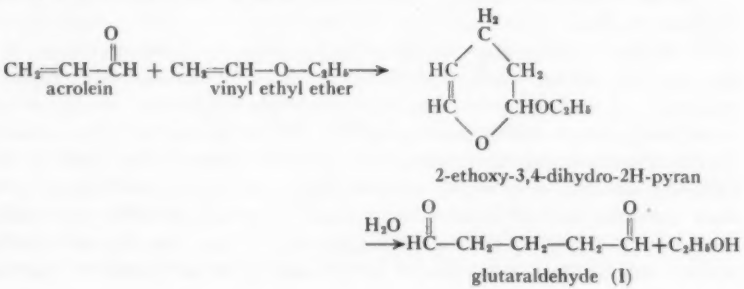
$$\frac{N}{4A}(V\text{-}V^1) = \text{millimoles of aldehyde in sample}$$

N = normality of thiosulfate
V = volume of thiosulfate to titrate blank
V^1 = volume of thiosulfate to titrate sample
A = number of aldehyde groups in molecule

The procedure outlined above was followed in analyzing tanning solutions at pH 5 or below. Samples from tanning solutions with a pH above 5 were acidified. This was done immediately after the addition of 10 ml. of distilled water mentioned at the beginning of the above analytical procedure. The acid (1*N* H_2SO_4) was added dropwise to a pH of 4. The number of drops of acid required was determined on a separate accurately measured sample, using a pH meter. The acidified samples were then analyzed as described above. The results are shown in Table I and Figs. 1 to 10.

DISCUSSION

Glutaraldehyde is a five-carbon dialdehyde of relatively simple structure (I) commercially available as a stable 25% aqueous solution. It was first reported by Harries (12) in 1908 but remained a laboratory curiosity until recent years when feasible processes were developed for its preparation. A recent publication (13) outlines the synthesis of glutaraldehyde, based on acrolein, in a two-step process. Acrolein is interacted with vinyl ethyl ether in a typical Diels-Alder reaction to produce an ethoxy dihydro pyran. This latter is then hydrolyzed with water to form glutaraldehyde and ethanol. This synthesis is outlined below:



Because of its ready availability and chemical reactivity, glutaraldehyde is a new product of the chemical industry which shows promise.

In our previous study, an estimate of the tanning power of glutaraldehyde and its comparison with other aldehydes was based on shrinkage temperature data obtained with small pieces. This, at best, was qualitative, and it was necessary to collect more scientific data concerning the rate of tanning. For this purpose it was decided that the rate of disappearance of aldehyde in the tanning liquor offered the most elegant and simplest approach to the determination of the over-all tanning rate. It was further desirable to use an entire skin in these studies in order to provide data more valuable to the tanner than similar data obtained with hide powder or small pieces of skin. This approach offers further advantage in averaging the factors of variability of the skin and enables interpretation of results from a theoretical as well as practical standpoint.

In these studies, therefore, an entire degreased pickled Syrian sheepskin of commerce was tanned with glutaraldehyde with pH and concentration as the principal tanning variables. Comparisons were made with formaldehyde and glyoxal. No pretense is made that these data are directly translatable to tannery-scale operations, since other well known factors such as mechanical action and buildup of heat enter into consideration. However, comparisons within experiments are justified.

A striking feature of the data in Table I is the rapid disappearance of glutaraldehyde and its approach to complete exhaustion when tanning was carried out under certain conditions. The data in Table I were calculated to give the percent of unreacted glutaraldehyde, and this was plotted against time to give the curves shown in Figs. 1 to 10. An advantage of the plot in this form is that fixed aldehyde expressed as percent of the drained pickled weight is readily calculated. The slope of these curves can be interpreted as a measure of the rate of tanning. In these figures the rate of change in Ts is also shown.

The rate of tanning at pH of about 2 was relatively slow, and as shown by Fig. 1 only about 5% of the glutaraldehyde was fixed in the first half hour. Thus, equilibrating the pickled skin for ½ hour before determination of the initial aldehyde concentration introduced only a small error (of the order of 5%). Interestingly enough, half of the glutaraldehyde charged was fixed by the skin in 24 hours, and Ts was gradually raised to 70°–75°C. even at this low pH.

The rate of tanning, as expected, increased rapidly with increase of pH, as indicated by the slope of the curves in Figs. 1 to 6. The maximum shrinkage temperature also was rapidly attained, and at the higher pH range (Figs. 5 and 6) was essentially reached in one hour. In general, fixation of aldehyde continued beyond this point but did not appear to contribute to

elevation of the shrinkage temperature. In the pH range of 4 to 5 (Figs. 2 and 3) equilibrium was not reached in the 24-hour period studied, although in the case of the lowest concentration (6% of the drained pickled weight and pH of 5) 90% of the glutaraldehyde was consumed in 24 hours. In the case of 6% glutaraldehyde, exhaustion of the glutaraldehyde was practically complete at pH 6 and above. At the 12% glutaraldehyde level, uptake of the aldehyde at pH above about 6.5 was 90 to 97% of that charged.

The rate of tanning in the pH region of 9 to 10 was complicated by disappearance of glutaraldehyde due to pH effects alone as shown by the blank in Fig. 6. Thus, in the blank run, half of the glutaraldehyde was destroyed in 3 hours at this pH.

In the comparable tanning run (12% glutaraldehyde in Fig. 6), disappearance of glutaraldehyde was extremely rapid, and the rate of tanning was evidently considerably higher than the rate of destruction of glutaraldehyde. Thus, purely from the rate standpoint, tanning took preference over the side reactions despite the relative instability of glutaraldehyde under these conditions. As shown in Fig. 8, glyoxal was less stable than glutaraldehyde under these pH conditions. The instability of glyoxal in alkaline solutions is well known and is discussed by previous investigators (1, 14, 15). Under the conditions of our experiments, half of the glyoxal disappeared in 2 hours at pH of 9 to 10. These two aldehydes were stable in the pH region below about 8, and formaldehyde was stable at all pH values (4.5 to 10.5) investigated.

Figure 7 shows the rate of tanning data obtained with formaldehyde when the concentration, on an aldehyde basis, was equivalent to 12% glutaraldehyde. On a molar basis the concentration in the case of formaldehyde corresponded to twice that of the glutaraldehyde. The important conclusion drawn from this figure is that the formaldehyde was far from exhausted at any of the pH levels studied, i.e., 5, 8, and 10. The unused formaldehyde ranged from 50 to 65% of that charged, in contrast to the high proportion fixed in the case of glutaraldehyde. The rate of attainment of maximum Ts was also lower in the case of formaldehyde.

The rate of tanning with glyoxal is shown in Fig. 8. In accordance with Gustavson's conclusion from shrinkage temperature data (14), there was no fixation of glyoxal at a pH of about 5. A gradual fixation of aldehyde and increase in Ts was noted at pH of about 8.

A comparison of these three aldehydes at a pH of about 8 and at a concentration equivalent to 12% glutaraldehyde is shown in the plot of Fig. 9. As judged by the slope of the curves, the rate of tanning increased in the order: glyoxal, formaldehyde, glutaraldehyde. The rate of increase in Ts also followed this same order. Only in the case of glutaraldehyde was exhaustion of aldehyde from the tanning liquor noted.

Comparison of these three aldehydes at pH 5 is shown in Fig. 10. The same general conclusions regarding reactivity were reached. No fixation of glyoxal was apparent. Approximately 70% of the glutaraldehyde was fixed, whereas formaldehyde was intermediate between these two.

Tanning was effected over a wide pH range. Based on the drained pickled weight, as little as 6% of the 25% aqueous glutaraldehyde solution, or 1.5% of actual glutaraldehyde, was sufficient to effect tanning and to elevate the Ts to 78°C. or above. Important properties from the tanning standpoint were the rapid tanning action and the fact that the aldehyde may be virtually completely exhausted from the tanning liquor.

ACKNOWLEDGMENT

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Editor's Note: The discussion will appear with Part II.

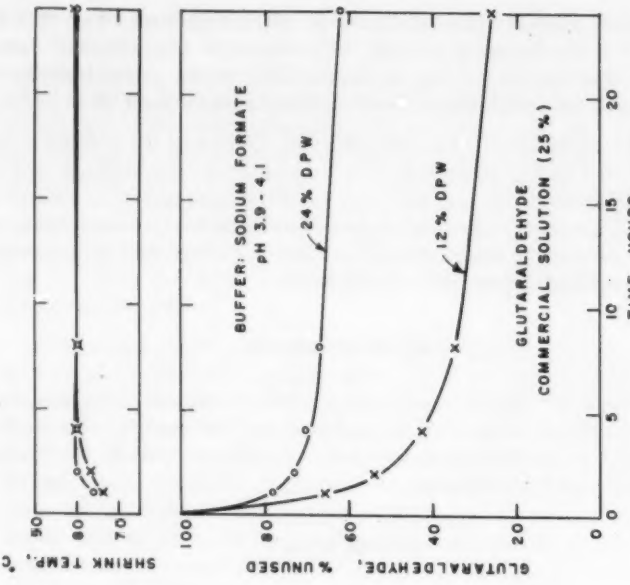

FIGURE 2.—Tanning rate with glutaraldehyde, pH 3.9–4.1

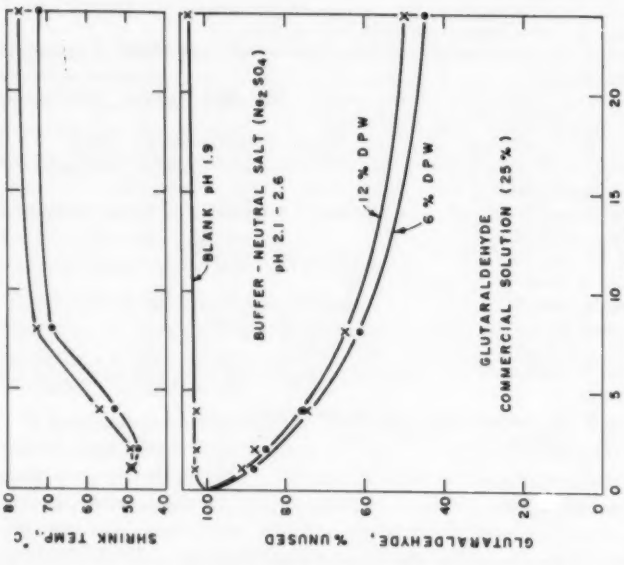

FIGURE 1.—Tanning rate with glutaraldehyde, pH 2.1–2.6

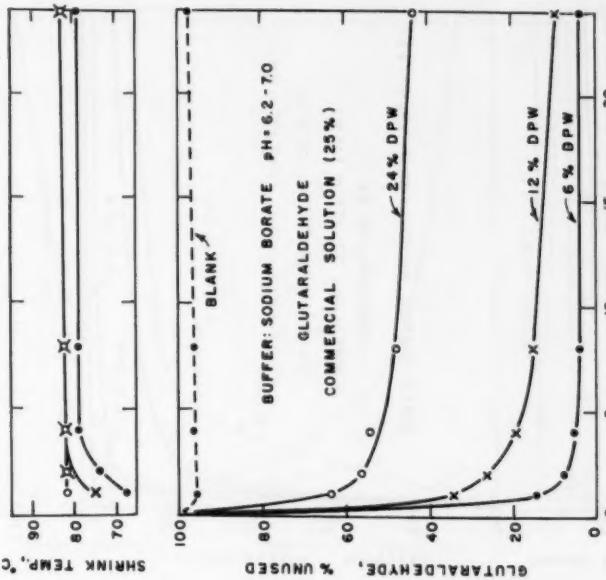

FIGURE 4.—Tanning rate with glutaraldehyde, pH 6.2–7.0

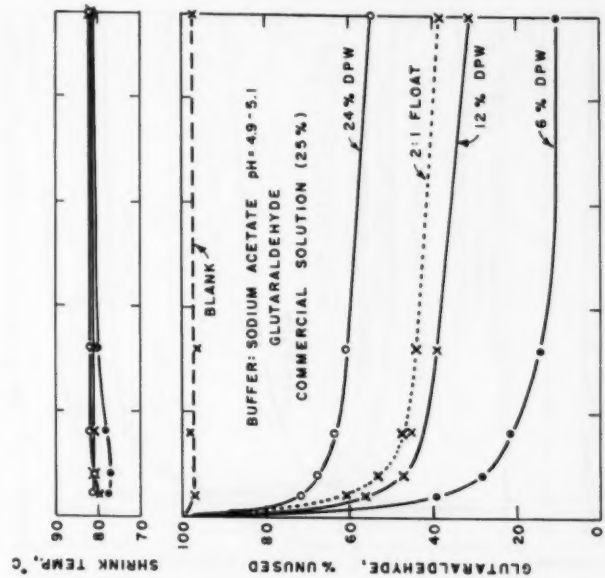

FIGURE 3.—Tanning rate with glutaraldehyde, pH 4.9–5.1

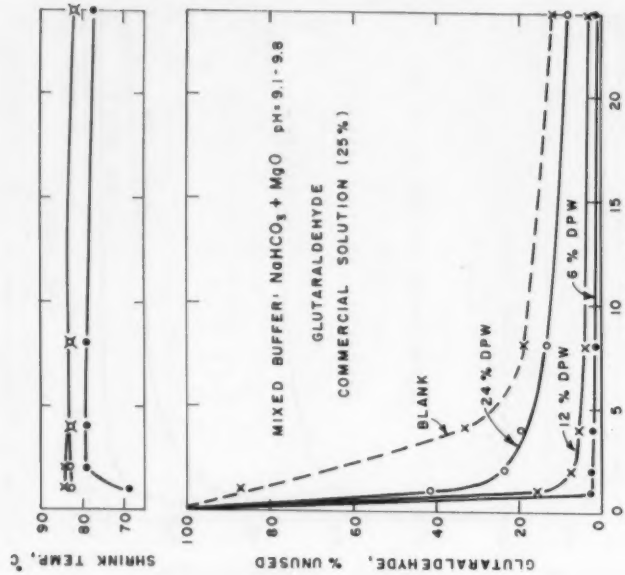

FIGURE 6.—Tanning rate with glutaraldehyde, pH 9.1–9.8

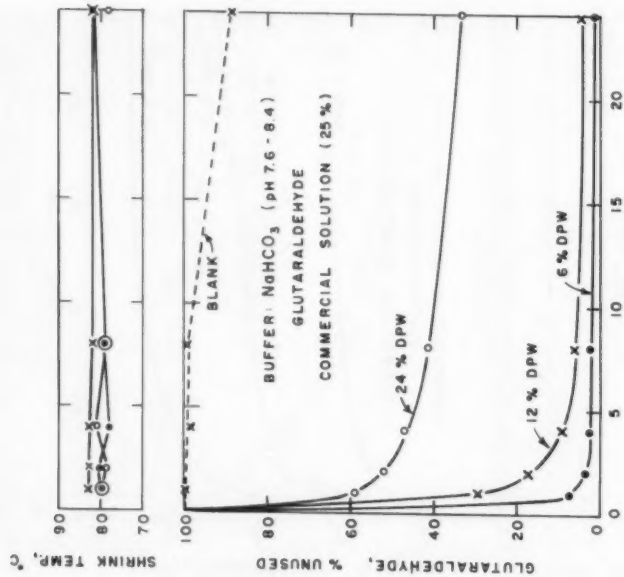

FIGURE 5.—Tanning rate with glutaraldehyde, pH 7.6–8.4

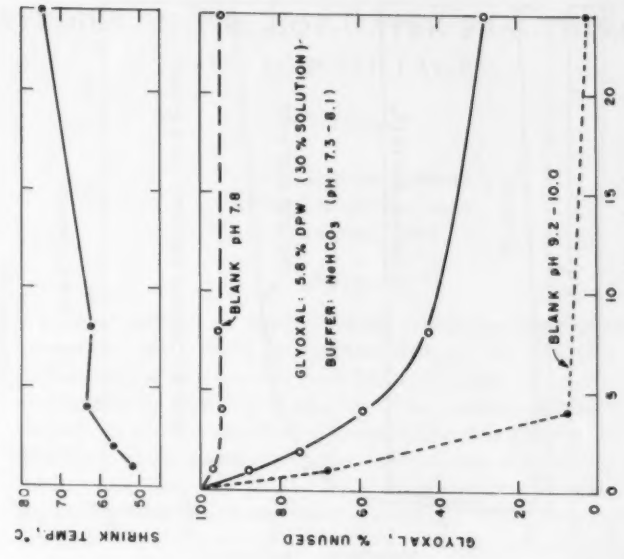

FIGURE 8.—Tanning rate with glyoxal

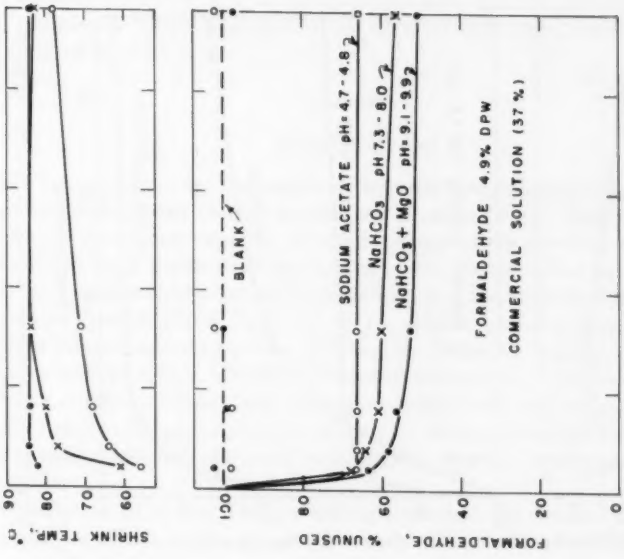

FIGURE 7.—Tanning rate with formaldehyde

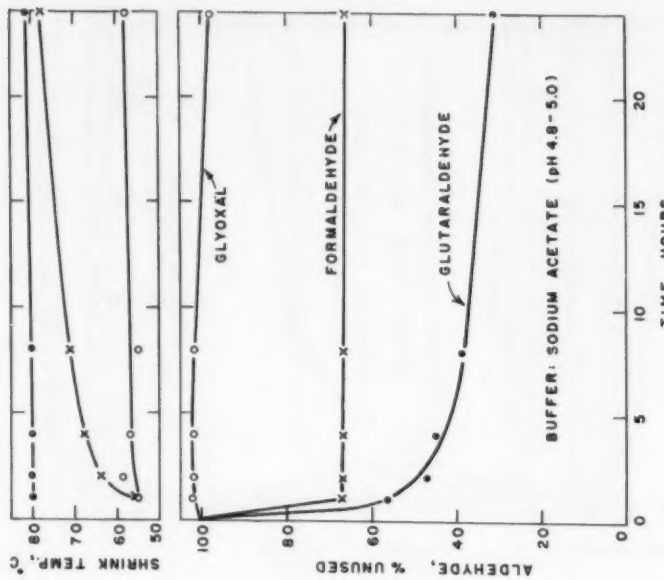

FIGURE 10.—Comparison of rates of tanning at pH 5 (approximately)

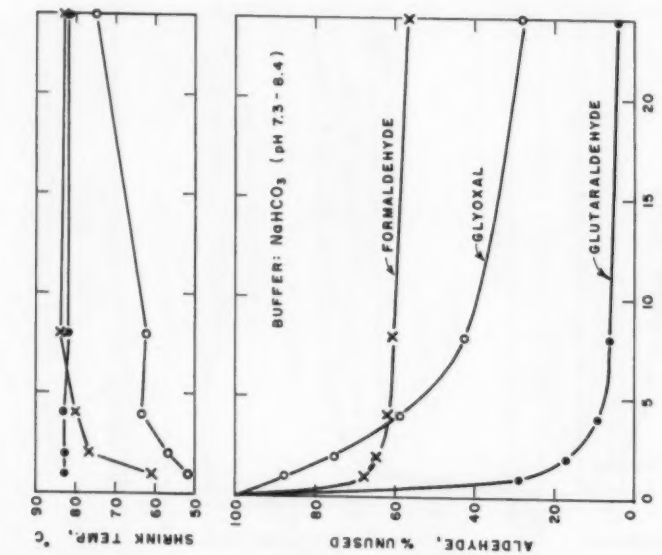

FIGURE 9.—Comparison of rates of tanning at pH 8 (approximately)

STUDIES ON THE HOT-WATER FRACTIONATION OF DNP COLLAGEN

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ABSTRACT

Fibrous collagen of bovine corium which has been purified by extractions with NaCl, phosphate, and citrate solutions differs on histological examination from fibrous collagen of bovine corium extracted only with NaCl solution. The 2,4-dinitrophenyl (DNP) derivatives of the two collagen preparations also differ in hot-water solubility, in the paper-electrophoretic patterns of their hot water–soluble fractions, and in the number of N-terminal amino acids present in their hot water–soluble fractions. Both the soluble and insoluble fractions of the two DNP collagen preparations have essentially the same ratio of nitrogen to hydroxyproline. The insoluble fractions of both preparations form on hydrolysis a DNP compound which appears to be of a carbohydrate nature and related to sialic acid.

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INTRODUCTION

The best evidence to date supports the view that collagen is a triple helix of polypeptide chains twisted around one another (1–4). Sanger's work on insulin (5) has shown that the structure of multichain proteins may best be determined by a preliminary separation of the chains before an attempt is made to do sequence studies on the amino acids of the individual chains. The finding of Boedtker and Doty (6) that a soluble collagen from carp swim bladder dissociated into its three polypeptide chains on heating in dilute salt solution indicated that a similar hot-water treatment of the bovine corium collagen might be tried. Such treatment would have the advantage that it would not involve any extensive changes in the polypeptide chains, such as would take place with the usual more drastic chemical treatments for chain separation.

In order to determine whether the separation of the chains had occurred, it would be advantageous to work with 2,4-dinitrophenyl (DNP) collagen,

*Ernest Griess Fellow

in which the N-terminal amino acids of the chains (those amino acids with the free amino groups at the end of the chains) had been tagged with the yellow 2,4-dinitrophenyl group by reaction with 2,4-dinitrofluorobenzene. Since three N-terminal amino acids have been found in collagen (7), the absence of any one of these in one of the fractions might indicate that some separation had been achieved.

The first hot water–fractionation experiments of DNP collagen were undertaken with a preparation from a collagen which was essentially bovine corium extracted with NaCl solution. When the hot water–fractionation experiments were repeated with a DNP collagen prepared from bovine corium which had been extracted with 5% NaCl solution, 0.1*M* Na_2HPO_4, and 0.1*M* citrate buffer (pH 3.6), the results of the fractionation differed from those obtained with the first DNP collagen preparation. Parallel studies were therefore carried out on the two DNP collagen preparations.

EXPERIMENTAL METHODS

Collagen preparations

(*a*) The NaCl-extracted collagen prepared by a modification of the Tancous method was the same as that previously used (7).

(*b*) The NaCl, phosphate, and citrate-extracted collagen was prepared in the following way. A steerhide was cut into 20 pieces (10 cm. x 60 cm.), the hair was clipped, excess flesh was removed, and the pieces were placed in a freezer within 1 hour *post mortem*. When the pieces were frozen (4 hr.), they were fleshed on a splitting machine. They were then placed in the freezer overnight. Corium splits were obtained the next morning by removal of the grain layer on the splitting machine and were cut into 1-cm. squares. The squares were extracted 4 times with 5% sodium chloride, 3 times with 0.1*M* Na_2HPO_4 (to remove mucoids and "alkaline buffer–soluble collagen"), 1 time with 0.1*M* citrate buffer (pH 3.6) (to remove "acid citrate–soluble collagen"), and 2 times with water. One of the extractions with each type of extracting solution involved an overnight period (16 hr.); the rest of the extractions were for shorter periods (approximately 4 hr.). All extractions were carried out at 7° C. with stirring, except that stirring was not continuous during the whole of the overnight periods. The total time of the extractions with these solutions was 4 days. The squares were then covered with acetone and allowed to stand at room temperature. The acetone was replaced by fresh acetone every 6 hr., until its specific gravity did not change after 6-hr. contact with the squares. The squares were then covered with ethyl alcohol and allowed to stand at room temperature 4 hr. They were similarly treated with diethyl ether and were then air-dried. This collagen preparation contained on the dry basis 18.32% nitrogen and 13.27% hydroxyproline.

This nitrogen value is higher than that of many other collagen preparations, although it is lower than the value of 18.42% reported by Veis and Cohen (8a) for an apparently highly purified collagen.

(*c*) A third collagen preparation, used only in the histological examination, was prepared essentially the same as the second preparation except that the extractions with phosphate were omitted, and three (instead of one) extractions with citrate buffer (0.1*M*, pH 3.6) were made.

Histological examination.—Histological examinations of the three collagen preparations were made after fixing with formaldehyde or with formaldehyde containing 12% NaCl and staining with haematoxylin and eosin.

Preparation of DNP collagens.—The collagen preparations were cut into approximately 3-mm. squares and were dinitrophenylated by the method previously used (7).

Hot-water-fractionation studies

(*a*) *Preparation of solutions.*—Since the DNP collagen prepared from the NaCl-extracted collagen did not appear to dissolve on heating for 1 hr. in water at 70°C., a higher temperature was used in the extraction experiments. Five to 15 g. of each of the DNP collagen preparations was heated at 90° C. with water for 2 hr. The ratio of DNP collagen to water was 1:100. Water lost by evaporation was replaced. The yellow solution was then poured through a filter paper to remove any floating fibers, and the filtrate was kept in the refrigerator until analyzed (Fraction 1). The same volume of water was again added to the residual squares, and they were again extracted at 90° C. for 2 hr. The second solution (Fraction 2) was treated as the first. Both solutions gelled at 7° C. The residual insoluble squares were air-dried and weighed.

(*b*) *Analysis of solutions and of residual squares.*—Aliquots of Fractions 1 and 2 and of the residual squares were used for analyses of total nitrogen and hydroxyproline. A modified Kjeldahl method was used for the nitrogen determinations, in which salicyclic acid and sodium thiosulfate were added in order to include the nitrogen of the dinitrophenyl group. The hydroxyproline analysis was carried out after hydrolysis for 8 hr. with 6*N* HCl by a modification of the Neuman-Logan method (8b).

(*c*) *Determination of DNP-amino acids in Fractions 1 and 2 and in the residual squares.*—To the remaining portions of Fractions 1 and 2 was added sufficient concentrated HCl to make the solutions 2*N*. The solutions were then refluxed for 4 hr. After hydrolysis they were cooled and extracted exhaustively with diethyl ether. The combined ether extracts were evapor-

ated to dryness at room temperature, and the residue was then chromatographed by the method of Green and Kay (9) on silicic acid–Celite (2:1) columns with various mixtures of organic solvents as developers for the identification of the DNP amino acids present in the original solutions. The remainder of each of the insoluble fractions was added to 2*N* HCl (ratio of squares to acid = 1:10) and hydrolyzed for 4 hr., and the hydrolyzate was worked up in the same way as the hydrolyzates of Fractions 1 and 2.

(*d*) *Paper electrophoresis.*—Fractions 1 and 2 from the two DNP collagen preparations were analyzed by paper electrophoresis. Since the positions of the components on the paper were to be determined by their yellow color, it was necessary to concentrate the solutions before electrophoresis. A sufficient amount of the concentrated solution for electrophoresis could easily be obtained by keeping 0.5 to 1 ml. of the original solution overnight in a desiccator over $CaCl_2$. Paper electrophoresis was carried out with a Spinco Model R Paper Electrophoresis cell. Borate buffer (pH 9.3, containing 7.63 g. $Na_2B_4O_7 \cdot 10H_2O$ and 0.62 g. boric acid per 1.) was used. The current was 2.5 milliamperes, and the time of the run was 6 hr.

EXPERIMENTAL RESULTS

Histological examination.—The collagen fibers of the preparation which had been extracted with NaCl solution were normal in appearance. In the preparation which had also been extracted 3 times with citrate solution, the collagen fibers were gelled. In the preparation which had also been extracted 3 times with phosphate solution and 1 time with citrate solution, the fibers were somewhat gelled, but not so much as in the previous preparations. It is obvious, then, that citrate (and possibly also phosphate) causes gelation of the collagen fibers.

Analytical results.—On the average the DNP collagen preparation from the collagen which had been extracted with NaCl, phosphate, and citrate solutions was more soluble in hot water than that prepared from NaCl-extracted collagen. While the amounts dissolved varied somewhat in each experiment, on the average 39% of the DNP collagen had dissolved in the first case in Fractions 1 and 2 and only 21% in the latter.

These results agreed with those obtained from the nitrogen determinations, which showed, on the average, 36 and 22% of the total nitrogen dissolved in Fractions 1 and 2. This finding of a difference in solubility in the preparations is not unexpected in view of the histological evidence that the collagen fibers were partially gelled in the preparation which was citrate-extracted but were normal in the NaCl-extracted preparation.

The protein of Fraction 1, of Fraction 2, and of the insoluble residue of the DNP collagen from the NaCl-, phosphate-, and citrate-extracted collagen

contained on the average 11.2, 11.5, and 12.0% hydroxyproline respectively. (The amount of protein in each of the fractions was calculated on the basis of the total nitrogen analysis, on the assumption that the protein contained 18% nitrogen.) With a similar method of calculation, and on the basis of a single experiment with the DNP collagen from the NaCl-extracted collagen, the protein of Fraction 1, of Fraction 2, and of the insoluble residue contained 11.4, 11.8, and 11.7% hydroxyproline respectively.

N-terminal DNP amino acids.—The N-terminal DNP amino acids found in each of the three fractions of the two DNP collagen preparations are shown in Table I.

TABLE I

DNP AMINO ACIDS FOUND IN HYDROLYZATES OF FRACTIONS FROM DNP COLLAGEN

Fraction	NaCl-extracted Collagen	NaCl-, Phosphate-, and Citrate-extracted Collagen
1 (soluble in hot water in 2 hr.)	serine aspartic acid	serine aspartic acid glycine
2 (soluble in hot water in 2–4 hr.)	serine aspartic acid glycine	serine aspartic acid glycine
residue (insoluble in hot water after 4 hr.)	serine aspartic acid glycine* (unknown slow-moving DNP compound)†	serine aspartic acid glycine (unknown slow-moving DNP compound)†

*In two experiments, no DNP glycine was observed in this fraction.
†The unknown slow-moving DNP compound observed in the hot water-insoluble residue of the two DNP collagen preparations is identical with the compound previously observed (7); its properties will be more fully discussed in the next section.

Unknown slow-moving DNP compound.—The hydrolyzates of the hot water-insoluble residues from the fractionation of the two DNP collagen preparations contained an unknown DNP compound. This compound appears on a silicic acid-Celite (2:1) column after development with 3½ volumes of acetic acid-acetone-ligroin (8:4:88) and 3½ volumes of acetic acid-acetone-ligroin (10:5:85) according to the Green and Kay (9) procedure for preliminary separation of DNP amino acids into groups before their

complete identification. All other DNP amino acids except DNP cystine run faster than the compound. DNP cystine runs slightly slower.

Although DNP cystine would not be expected to be present in the preparation, since cystine is absent from collagen, the possibility that it might have occurred in the preparations as an impurity existed. The DNP derivative of cystine was therefore prepared and compared in chromatographic behavior and in solubility in ether and in water with the unknown DNP compound. The DNP derivative of homocystine (10) was similarly prepared and compared with the unknown. However, neither of these compounds had properties agreeing with those of the unknown DNP compound.

Green and Kay (9) have also shown that a slow-moving DNP compound in this position on the column may be a DNP peptide. Accordingly the unknown DNP compound was eluted from the original column, again hydrolyzed for 4 hr. in 2*N*HCl, and rechromatographed as in the original column. Its chromatographic behavior was unchanged by this procedure. Since a DNP peptide would probably have been at least partially hydrolyzed during the additional hydrolysis, the DNP compound did not behave as a typical peptide. If it were a DNP peptide, it would be unusually resistant to hydrolysis.

A third possibility was that the compound was a DNP amino sugar. Two amino sugars, glucosamine and galactosamine, present in skin as the N-acetyl derivatives in hyaluronic acid and chondroitin sulfate and possibly in other forms, are known to form dinitrophenyl derivatives. Accordingly DNP glucosamine and DNP galactosamine were prepared by treatment of the respective amino sugars with 2,4-dinitrofluorobenzene in sodium bicarbonate solution as in the Sanger procedure (11). The behavior of these two DNP amino sugars on chromatography on the silicic acid–Celite columns by the Green and Kay method (9) was similar to but not identical with that of the unknown, as they were slower moving than the unknown with the second solvent used in the development (acetic acid–acetone–ligroin [10:5:85]). The unknown DNP compound differs further from the DNP amino sugars in being more soluble in ethyl acetate and less soluble in water.

Since the unknown DNP compound was, therefore, not identical with any of the more obvious possibilities, a more thorough investigation of its properties was undertaken. A method of preparation of the DNP compound which provided larger amounts than could be obtained from elution of the silicic acid–Celite column was developed for these tests. A hydrolyzate of DNP collagen (prepared by 4 hr. refluxing with 2*N*HCl) was extracted with ether, the ether extract was extracted with water to separate the more water-soluble DNP compound from the more ether-soluble DNP amino acids, the water extract was then exhaustively extracted with ether to remove any DNP amino acids which might have dissolved to a slight extent in the aqueous phase, the water extract was then exhaustively extracted with ethyl acetate

to remove the unknown DNP compound, and the ethyl acetate extract was concentrated to dryness at room temperature. The yellow solid obtained in this way was shown to be identical with the unknown DNP compound from the silicic acid–Celite column by comparative chromatography.

The DNP compound is somewhat soluble in ether, but it is even more soluble in water. These solubility characteristics suggest that the compound is related to the carbohydrates, since the large number of hydroxyl groups of the latter group of compounds would be expected to increase the solubility in water of DNP derivatives. It is even more soluble in 0.1*N* Na_2CO_3 than in water, a fact which suggests that the compound has acidic properties. It is very soluble in ethyl acetate.

The DNP compound gives a positive test for a reducing sugar with ammoniacal silver solution (12). The ultraviolet and visible absorption spectra of the DNP compound, as well as of DNP glucosamine and DNP galactosamine, were determined in 0.1*N* Na_2CO_3 solution with a Beckman quartz spectrophotometer. While the DNP glucosamine and DNP galactosamine had absorption maxima in the 360–380 mμ region, as is to be expected for a compound with the nitrogen of the amino group substituted by the DNP group, the unknown DNP compound did not have a maximum in this region but had an inflection at approximately 300 mμ. This type of spectrum suggests that an O-DNP group (rather than an N-DNP group) is present in the unknown DNP compound (13).

A search of the literature for naturally occurring compounds whose DNP derivatives might have properties agreeing with those of the unknown DNP compound suggested the recently investigated "sialic acid" as a possibility. "Sialic acid" is a collective term for the acylated derivatives of neuraminic acid—$CH_2OH(CHOH)_3CHNH_2CHOHCH_2COCOOH$. Up to the present time four different sialic acids have been crystallized, differing in the nature and extent of the substitution on the nitrogen of the amino group or on the oxygen atoms of the hydroxyl groups in the neuraminic acid structure. The hexosamine moiety of N-acetylneuraminic acid is D-mannosamine (14). Sialic acid is present in human serum (60 to 66 mg. per cent), partially, at least, in combination with serum proteins, and has been recently found to occur in a large proportion of animal mucoproteins and mucopolysaccharides. For example, bovine submaxillary gland mucosubstances give on partial hydrolysis with alkali a disaccharide composed of sialic acid and an anhydro-N-acetylgalactosamine (15).

DNP substitution of an oxygen atom in sialic acid could possibly occur if the compound were present in enolic form—$CH_2OH(CHOH)_3CHNH_2$-$CHOHCH=COHCOOH$—under the conditions used for dinitrophenylation. This hydroxyl group, with its adjacent double bond giving it partial phenolic character, might undergo substitution in a process similar to the dinitropheny-

lation of the phenolic group of tyrosine which takes place in the Sanger reaction.

The unknown DNP compound, when tested, showed some properties expected of a compound related to sialic acid. It gives off a gas and forms humin when it is heated with strong mineral acid. This behavior is characteristic of sialic acid. Some decomposition of the DNP compound from this reaction probably takes place in the course of its preparation by the hydrolysis of DNP collagen; however, since the acid used in the hydrolysis is dilute (2*N* HCl), probably extensive decomposition does not occur. It has been shown that sialic acid can be split off from some mucosubstances by boiling under quite mildly acid conditions.

The unknown DNP compound was tested for sialic acid by the diphenylamine reaction of Dische (16). In this procedure the absorption at 530 mμ of the reaction product is measured to determine the sialic acid content. When the unknown was tested with this reaction, it had a strong absorption at 530 mμ. However, the color of the solution was green; unsubstituted sialic acid is reported to give a purple color in this reaction. Possibly the presence of the DNP group in the sialic acid might modify the chromophore sufficiently to cause a shift in the color from purple to green; or possibly there is a sufficient amount of the original unreacted yellow material present to cause a shift to the green color; or possibly the unknown compound is not DNP sialic acid but is related to it.

If the unknown DNP compound is DNP sialic acid, then sialic acid must be present in the original collagen preparation used for the preparation of the DNP collagen. Therefore, a positive Dische diphenylamine test should be obtained with the collagen preparation. Accordingly, a sample of the Na-, Cl-, phosphate-, and citrate-extracted collagen was refluxed with 2*N* HCl for 4 hr. The solution of partially hydrolyzed collagen which resulted gave a purple color with high absorption at 530 mμ. On the basis of this test, this collagen preparation contains sialic acid or a closely related compound.

It cannot be decided from these experiments whether the sialic acid (or related compound) is a component of the collagen molecule or of another substance which is present in the skin and which was not removed from this collagen preparation. The sialic acid (or related compound) must be present in a combined form in the collagen preparation, bound either to another carbohydrate constituent or to protein, and must be released on hydrolysis, since the unknown DNP compound is not lost by solution in the water during the extensive washing that the DNP collagen undergoes before hydrolysis, although the unknown compound is very soluble in water.

Paper electrophoresis.—From the paper-electrophoretic patterns of Fractions 1 and 2 of the DNP collagens (Table II) it is evident that the hot water-soluble fractions obtained from the DNP collagen prepared from the

TABLE II

POSITIONS OF YELLOW BANDS AFTER PAPER ELECTROPHORESIS OF HOT WATER–SOLUBLE FRACTIONS OF DNP COLLAGEN

DNP Collagen Prepared from			
NaCl-extracted Collagen		NaCl-, Phosphate-, and Citrate-extracted Collagen	
Fraction 1	Fraction 2	Fraction 1	Fraction 2
1. center 2. 56 mm. to + pole	1. center 2. 58 mm. to + pole	1. center	1. center

NaCl-extracted collagen differ from those obtained from the NaCl-, phosphate-, and citrate-extracted collagen.

The "center" positions indicate that the material had not formed a band away from its point of application at the center of the paper strip, although the band itself may have greatly widened during the run. The fact that only one spot appears on a paper does not necessarily indicate that only one substance is present in the fraction. It may mean that separation of the components has been incomplete under the conditions of the run.

DISCUSSION

The evidence from histological examination, paper electrophoresis, and data on N-terminal amino acids clearly shows that fibrous collagen from bovine corium which has been extracted with NaCl, with 0.1*M* Na_2HPO_4, and with 0.1*M* citrate buffer (pH 3.6) differs from a similar collagen which has been extracted only with NaCl solution. The view that fiber degradation occurs on citrate extraction is in agreement with the work of Schmitt, Gross, and Highberger (17), which showed, on the basis of electron microscopic examination, that a portion at least of the collagen extracted by citrate is derived from the formed fibrils, which appeared disorganized after the treatment. The present data also indicate that attempts to remove "alkaline buffer–soluble" and "acid citrate–soluble collagen" from a fibrous collagen preparation by extraction with 0.1*M* Na_2HPO_4 and with 0.1*M* citrate buffer (pH 3.6) result in a poor collagen preparation from the standpoint of degradation of the fibers.

In both DNP collagen preparations the residue which is insoluble after 4 hr. heating in water at 90° C. contains a carbohydrate-like moiety, whereas those portions which dissolved do not contain this carbohydrate material. If it is assumed that this carbohydrate-like substance is an integral part of

the collagen molecule (a point which has not been proved in these experiments, however), then it is interesting to speculate on its importance in rendering the collagen fiber into an insoluble form. The view has often been advocated (18, 19), based especially on the fact that mucopolysaccharides are present in abundance during fibrogenesis of collagen in connective tissue, that mucopolysaccharides stabilize the fiber structure of collagen. Bowes, Elliott, and Moss (20) have also suggested, on the basis of chemical differences in the analyses of acid-soluble collagen of bovine skin and of the insoluble collagen, that acid-soluble collagen differs from the insoluble form chiefly in that the latter is associated with a material (possibly a protein-mucopolysaccharide complex) which stabilizes it.

Highberger, Gross, and Schmitt's work (21) on the precipitation of soluble collagens from solution is also an indication that the collagen may be rendered insoluble by carbohydrate-containing material, as many of the precipitating agents, such as acid glycoprotein, chondroitin sulfate, thrombin, heparin, adenosine triphosphate, ribonucleic acid, deoxyribonucleic acid, and gum arabic, contain carbohydrate moieties. (Acid glycoprotein and prothrombin are known to contain sialic acid.) In reticulin it has also been found that the hot water–soluble portion does not contain carbohydrate but that the insoluble portion gives positive carbohydrate reactions (22). Grassmann (23) has also emphasized that carbohydrate is necessary for cross-banding in collagen.

On the other hand, Schmitt, Gross, and Highberger (17) obtained a purified skin collagen preparation of unweakened structure which contained only very small amounts of hexose and hexosamine. Possibly, however, in this case exhaustive extractions with one-half saturated $Ca(OH)_2$ solutions used in the preparation of this collagen might have caused the carbohydrate to be converted by reaction in the alkaline medium to compounds no longer giving typical carbohydrate reactions but still capable of stabilizing the structure. Evidence at hand at the present time does not warrant unreserved conclusions as to the role of carbohydrate in the collagen structure.

The hydroxyproline content of the protein of Fraction 1 of the DNP collagen from the NaCl-extracted collagen is essentially the same as that of the whole collagen molecule, although there are only 2 N-terminal amino acids present in the fraction instead of the 3 N-terminal amino acids found in whole collagen. This fact suggests that 2 chains have broken off from the 3-chained collagen molecule and that these chains contain approximately the proportion of hydroxyproline that is present in the molecule as a whole.

Work is continuing on the identification of the slow-moving DNP compound which is similar to sialic acid, on the composition of the extracts obtained in the purification of collagen, and on the composition of the hot water–soluble fractions.

SUMMARY

1. Fibrous collagen from bovine corium which has undergone extraction with NaCl, phosphate, and citrate solutions or with NaCl and citrate solutions shows gelation of the collagen fibers (partially in the first case and practically completely in the second) when examined in microscopic sections. Collagen which has undergone extraction only with NaCl solution does not show any gelation of the fibers microscopically.

2. DNP collagen prepared from collagen extracted with NaCl, phosphate, and citrate solutions dissolves in hot water to a greater extent than DNP collagen from collagen extracted only with NaCl solutions.

3. The hot water-soluble fractions from DNP collagen from NaCl-, phosphate-, and citrate-extracted collagen show different paper-electrophoretic patterns than those from DNP collagen from NaCl-extracted collagen.

4. DNP collagen from NaCl-extracted collagen is not soluble in water at 70° C. A fraction which is soluble on 2 hr. heating with water at 90° C. contains only two of the three N-terminal amino acids of collagen. A similar fraction from DNP collagen from a NaCl-, phosphate-, and citrate-extracted collagen preparation contains the three N-terminal amino acids.

5. Each of the three fractions obtained by hot-water fractionation of DNP collagen from each of the two collagen preparations shows approximately the same hydroxyproline/nitrogen ratio.

6. An unknown DNP compound obtained on hydrolysis of the hot water-insoluble residue of either of the DNP collagens prepared from the two collagen preparations has carbohydrate-like properties. On the basis of its color reactions with diphenylamine in acid solution, it appears to be related to sialic acid.

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Publication of a new booklet, "The Hide Futures Market", has been announced by Commodity Exchange, Inc., New York, trading center for futures contracts in hides, rubber, copper, tin, lead, zinc, and burlap. Harold A. Rousselot, Comex president, said the new publication delineates clearly the current hide contract and gives a full explanation of how hide futures are traded on Comex. Specific examples showing how the tanner, producer, and dealer can make use of the Exchange's hedging facilities are included. Single copies may be obtained by writing: Secretary, Commodity Exchange, Inc., 81 Broad St., New York 4, N. Y.

Corporations have become important contributors to the support of scientific research in academic institutions. By providing funds both for fellowships and for general support, they have greatly enhanced the independence and strength of private institutions. Many universities are able to select imaginative programs and support exceptional researchers by using uncommitted funds obtained from corporations. It is to be hoped that this support will not only continue but increase; for high quality research is one of the prime ingredients in the training of high quality manpower. If corporations support significant research, they will benefit directly from better trained manpower, and they will benefit ultimately from the store of knowledge they have helped to advance.

—*Strengthening American Science*, A Report of the President's Science Advisory Committee, Dr. J. R. Killian, Jr., *Chairman*. Dec., 1958.

LIFE LINES

Brief Biographies of Our Contributors

DR. CLARA DEASY—See the May, 1959, *Journal.*

MARTIN L. FEIN received his B.S. and M.S. degrees from Temple University. Before transfer to the United States Department of Agriculture in 1941, he worked with the Synthetic Fuel Group at the U. S. Bureau of Mines in Pittsburgh. From 1941 to 1953, at the U. S. Department of Agriculture's Eastern Utilization Research Branch, he studied the preparation and evaluation of various derivatives of lactic acid. In 1953 he transferred to the Hides, Tanning Materials and Leather Section of the same Branch, where is is conducting research on the chemical modification of hide substance.

DR. EDWARD M. FILACHIONE is Supervisor of the Hide Modification Unit of the Hides, Tanning Materials and Leather Section of the Eastern Utilization Research Branch, U. S. Department of Agriculture. He received his B. S. degree from the University of Illinois and his Ph. D. degree from Northwestern University. After six years of teaching and industrial research he joined the staff of the U.S.D.A.'s Philadelphia laboratory in 1941. His previous research and publications have been primarily in the field of organic synthesis. Since 1951 he has been conducting research in the field of leather chemistry. He joined ALCA in 1955.

EDWARD H. HARRIS, JR. obtained a B.A. degree from LaSalle College, Philadelphia, in 1950. He joined the Eastern Utilization Research Branch, U. S. Department of Agriculture, in 1942 and worked on lactic acid and its derivatives. In 1951 he was transferred to the unit on chemical modification of hide proteins in the Hides, Tanning Materials and Leather Section.

DR. JOSEPH NAGHSKI—See the April, 1959, *Journal.*

Oil tannage (German Sämischgerberei) is also called "chamoising". The equivalent German "sämisch" does not occur until about 1420, the Slavonic "zamscha" is even later. These words and the Dutch "zeem", French "chamois", were formerly believed to be related to the skin of the chamois, the mountain-goat of the Alps. However, it is much more probable that these words spring from an Arab sha'hm (Turkish semiz) fat.
—*Studies in Ancient Technology*, Vol. V. R. J. Forbes. Leiden: E. J. Brill, 1957.

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PAST PRESIDENTS

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. MCLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM, R. M. KOPPENHOEFER, H. G. TURLEY, E. S. FLINN, E. B. THORSTENSEN.

EMPLOYMENT NOTICES

ACADEMIC POSITION open for man with experience in Leather Chemistry and Leather Technology. Must have academic degree. Work interesting and rewarding. Opportunity for research and consulting. Excellent retirement benefits. Apply: Dept. of Leather Engineering, Lowell Technological Institute, Lowell, Massachusetts.

The South African Bureau of Standards (address Private Bag 191, Pretoria, Union of South Africa.) has two vacant posts available in the Leather and Footwear Division. They are:

1. Senior Technical Officer (*Footwear*). The minimum qualifications required are a B.Sc. degree or equivalent, and at least 9 years practical experience in the footwear industry. The commencing salary will be determined in accordance with qualifications and experience on the scale £1380x60-£1740. The duties will include the preparation of all types of footwear specifications and codes of practice, and supervising the laboratory testing of shoes and boots.

2. Technical Officer (*Leather*). The minimum qualifications required are a B.Sc. degree or equivalent, and at least 3 years specialized training or practical experience in leather chemistry. The commencing salary will be determined in accordance with qualifications and experience on the scale £1080x60-£1320. The duties will include taking charge of the testing laboratory and assisting in the preparation of standard leather specifications.

Anyone interested may submit his qualifications to, and obtain further information from, the above address or by writing to Dr. R. G. Shuttleworth, Scientific Attaché, c/o South African Scientific Liaison Office, 1907 K Street N.W., Washington 6, D. C.

COUNCIL MEETING MINUTES

June 14, 1959

Grand Hotel

Mackinac Island, Michigan

A meeting of Council was held with President Maeser presiding and Messrs. Henrich, Miller, Retzsch, Somerville, E. B. Thorstensen, Wederbrand, Wilson, Windus, and O'Flaherty present.

The minutes of the January 16 meeting were approved as published.

C. David Wilson reported on the papers submitted for the prize and presentation at the International Meeting. Four very good papers were submitted, and after very careful and lengthy deliberation the paper submitted by Dr. Lee P. Witnauer, of the Eastern Utilization Research Laboratory, U. S. Department of Agriculture, was unanimously selected. The other papers are

to be presented at the 1959 ALCA meeting. The title of the paper selected for presentation at the International Meeting is "Dynamic Electrical Behavior of Untanned Hide Containing Sorbed Water."

Council expressed its appreciation to the Awards Committee for its work.

President Maeser reported to Council that he was asking several of the officers to participate in the Presidential Address. This was done for the purpose of permitting the members to learn of the services rendered by the other officers. He also announced that Jerome Rogers, who has attended every meeting for 49 years, would be unable to attend this year.

Council approved President Maeser sending a wire of greeting to George Kerr, the first President of ALCA.

Dr. Henrich reported on the following changes in the technical committees:

Mineral-tanned Leather—R. J. Banner joined the committee and T. S. Perrin resigned.

Physical and Mechanical Properties—Charles Dudley and M. Bailey joined the committee. Arthur Kay resigned from Miscellaneous Physical Properties and Mr. Bailey will be the new chairman.

Vegetable Leathers—Arthur Kay resigned. A new chairman will be announced soon.

Upon a motion by Dr. Somerville, seconded by Mr. Retzsch, these committee changes were unanimously approved.

Mr. Wederbrand brought up the matter of the ALCA public address system. The Secretary was instructed to send a memorandum of this system to E. B. Thorstensen, who may have a buyer.

Mr. Wederbrand reported on the Hotel Lido on Long Island (30 miles from New York City). He and Mr. Retzsch were instructed to look into its suitability and report at the next meeting. Council suggested that the next Council consider the selection of French Lick, Indiana, for the 1962 annual meeting.

Mr. Thorstensen reported on the work of the Tannery Effluents Committee, which now recommends to Council that the methods which they have assembled be published in our Methods Booklet. Upon a motion by Dr. Henrich, seconded by Mr. Miller, Council unanimously approved the payment of $100 to the American Public Health Association for the privilege of using their methods. The Tannery Effluents Committee is to be retained on a stand-by basis.

Council then reviewed the file on the offer of the Salem Oil and Grease Company to establish an annual lecture. Upon motion made by Mr. Retzsch,

seconded by Mr. Miller, and unanimously approved by Council (Mr. Martin's vote came in a letter), it was agreed to accept the Salem Oil and Grease Company's offer to establish "The John Arthur Wilson Memorial Lecture" according to the arrangements set forth in President Maeser's letter to Council on April 17.

There being no other business, the meeting was adjourned at 10:45 P.M.

Respectfully submitted,

FRED O'FLAHERTY
Secretary

COUNCIL MEETING MINUTES

June 17, 1959
Grand Hotel
Mackinac Island, Michigan

The meeting was called to order by President Maeser at 12:40 P.M. Present were Messrs. Henrich, Tetreault, Somerville, Edmonds, Stubbings, Retzsch, and O'Flaherty.

The minutes of the June 14 Council meeting were read.

Dr. O'Flaherty read the election report from the Board of Tellers (T. C. Blair, Chairman, with George Shepard and Lorne Rayfield) advising that the following members were elected to Council for the years 1959–1961:

Frank Edmonds
Elwood Presley
Herbert Tetreault

The present Council welcomed the new members.

Dr. Henrich reported on the following additional changes in the Technical Committees:

Robert M. Lollar will assume chairmanship of the Vegetable Leathers Committee.

G. E. Daub resigned from the Hide Powder Committee. Council recommended J. F. Wagoner to this Committee.

Dr. Stubbings presented the following financial report of this Convention:

INCOME

Registration—Members	@$ 8.00 (258)	$2,064.00
Nonmembers	@$15.00 (38)	570.00
		$2,634.00
Exhibitors @$100.00 (9)		900.00
Total Income		$3,534.00

EXPENSES

Golf	$ 300.00
Ladies	300.00
Entertainment	300.00
President's Reception	1,000.00
Hotel Expense	150.00
Speaker	500.00
Total Expenses	$2,550.00

Dr. Stubbings advised Council that the attendance was very close in number to the meeting held at the same site in 1956.

Council considered both French Lick, Indiana, and returning to Mackinac in 1962. Dr. Stubbings talked to the Sales Manager at the hotel and obtained tentative dates of June 17–20, 1962. Council unanimously agreed that if these dates are available, the Association will return to the Grand Hotel in 1962.

Council confirmed to the Secretary that one free copy of the methods booklet may be sent to all members upon request.

Dr. O'Flaherty read a letter from Dr. Nayudamma requesting ALCA official approval of hide powder manufactured in India. Council agreed that Dr. Nayudamma may compare the approved ALCA hide powder to their product in order to certify theirs, but our Association could not test their hide powder to give it official approval.

With the International Meeting near, the Secretary requested Council to consider the ALCA representatives on the International Committee Commissions. Council recommended that the chairmen of the corresponding technical committees would be the ALCA representatives on the International Committee Commissions.

President Maeser, with Council's approval, appointed the following committees:

Awards Committee: Thomas Thorstensen, chairman, with Henry B. Merrill and F. Leslie Collins.

Nominating Committee: E. D. Compton, chairman, with Joseph R. Kanagy and Rolf Quarck.

Council agreed that the committees to select the Honor Lecturer would be composed of one member appointed by Salem Oil and Grease Company and two members appointed by the ALCA President, with one of these members being a Council Member. The committee to select the speaker in 1961 is Dr. Harold G. Turley, Chairman, with Dominic Meo and Elwood Presley. Mr. Maeser will write to Salem Oil and Grease Company and express Council's appreciation of their offer. Mr. Maeser will also write to Dr. Karl Gustavson and ask him to be the speaker in 1960.

Council suggested a certificate or scroll be presented to the Honor Lecturer. Mr. Maeser had a drawing prepared, which, after showing it to Council, he gave to Dr. O'Flaherty to obtain suggestions for having it adapted for this use.

Dr. Stubbings recommended that the Association buy a new slide projector for use at the annual meetings. Upon motion by Dr. Somerville, seconded by Mr. Retzsch, Council approved the purchase of a new slide projector to be paid for from the Convention Fund.

Dr. Henrich informed Council that in Method B5, "Total Nitrogen and Hide Substance," the committee agreed that a "warning note" should be added saying that nitrogen may be added to the leather through the use of certain resins, polymers, finishes, loading materials, and even tanning materials, and such nitrogen will usually appear as "hide substance" by this method.

George K. Kardos and Eijiro Sugano were elected to active membership. New associate members are David A. Burns, Tom F. Moore, James M. Petrie, John H. Reck, Charles Robertson, Charles Robson, K. L. Rue, Stanley Urban, E. John Koppany, and Robert A. Norton.

The next meeting of Council will be held on October 8 at the Tanners' Research Laboratory in Cincinnati, Ohio.

There being no further business, the meeting was adjourned at 1:50 P.M.

Respectfully submitted,

FRED O'FLAHERTY
Secretary

ABSTRACTS

A Systematic Study of Fungi on Tan Liquors. I. *Aspergilli.* V. S. Krishnamurthi and S. N. Sen. *Bull Central Leather Research Inst., Madras,* **5,** 213–19 (1959).—Four species (*A. nidulans, A. variecolor, A. carneus, and A. japonicus*) isolated from tan liquor are described. H.B.M.

Manufacture of Natural and Waxed Chrome Sole Leather on a Cottage and Small-Scale Level. M. A. Rama Iyer, K. Rajabathar, and K. T. Sarkar. *Bull. Central Leather Research Inst., Madras,* **5,** 220–22 (1959).—A description. H.B.M.

Observations on the Official Method for the Determination of Color Tolerances. H. E. Nursten. *J. Soc. Leather Trades' Chemists,* **43,** 50–58 (1959).—A critical review of the method for color tolerance is presented. Several amendments are suggested to the section dealing with measurement of chromaticity and luminance and to the section on calculation of color tolerance. J.M.C.

Supplementary Report of the Color Committee of the S. L. T. C. on Nursten's "Observations On the Official Method for the Determination of Color Tolerances". J. S. Mudd. *J. Soc. Leather Trades' Chemists,* **43,** 59–64 (1959).—A paper given in rebuttal to the criticism of Nursten. J.M.C.

Studies of Invertebrate Collagen Preparations. M. R. Watson and N.R. Silvester. *Biochem. J.,* **71,** 578–84 (1959).—The cuticle of *Ascaris lumbricoides* and the Cuvierian tubules of *Holothuria forskali* were examined. The presence of collagen in these tissues is evidenced by their wide-angle X-ray–diffraction patterns. Although their amino acid compositions are very different, they both have features which clearly relate them to vertebrate collagens. Both have hydroxyproline residues, a high content of glycine residues, and an infrared absorption band at 3330 cm^{-1}. Contrary to previous belief, collagen fibrils from the Cuvierian tubes of *Holothuria forskali* have 640 Å periodicities along the fibril axis. The shrinkage temperatures of the collagens studied cannot be directly related to their hydroxyproline contents. J.M.C.

A Quantitative Study of Fastness to Wet-Rubbing. C. H. Spiers and J. P. W. Burnett. *J. Soc. Leather Trades' Chemists,* **43,** 38–50 (1959).—The Satra machine was used to evaluate quantitatively the removal of the iron oxide pigment of a pigmented finish by the action of wet-rubbing. Damp pads with carefully regulated moisture contents were used to apply the wet-rubbing action to the sheepskin leathers. Pigment removal was estimated by determining iron content of the pads. The pigment in a casein-based pigmented finish was removed at a steady rate by wet-rubbing whether the finish was fixed or not. Several fixing agents ($HCHO\text{-}CH_3COOH$, HCHO—Cr alum, HCHO—Cr acetate) considerably improved resistance to wet-rub. Plating the leather with a casein

finish fixed with HCHO-CH_3COOH appeared to damage the outer layers of the finish while improving the inner layers. Resistance to wet-rub was increased by increasing the proportion of casein binder or by applying a top coat of casein season. Addition of a small amount of resin emulsion to a casein-based pigmented finish produced an outer abrasive-resistant pigmented resinous layer over the casein-based finish. Addition of larger amounts produced an outer pigment-free resinous layer beneath which is a resinous pigmented layer of greater resistance to wet-rub. J.M.C.

The Action of Ethylene Sulfide on Collagen. A. Gill. *J. Soc. Leather Trades' Chemists*, **42**, 394–403 (1958).—Small squares of oxhide, center-split collagen, were dried and immersed in dry ethylene sulfide. At room temperature 4 days were required for polymer deposition to reach a sufficient level to increase the shrinkage temperature. At 50° C. the immersion period was reduced to 24 hr. Deaminated, esterified, methylated and esterified, deaminated and esterified, and native collagen were reacted with ethylene sulfide in this manner. By introducing roughly 95% ethylene sulfide on a weight basis to native collagen, the shrink temperature was elevated from 60° C. to above 100° C. The reagent was also applied to air-dry pieces of untanned skin and to samples of a vegetable-tanned, a chrome-tanned, and three zirconium-tanned leathers. The shrinkage temperatures of skin and leathers were raised significantly by the procedure, and the water solubles in a light vegetable-tanned sole leather were reduced to near zero. Polymerization of the ethylene sulfide monomer within the fibrous matrix apparently accounts for the results. J.M.C.

The Methods and Mechanism of Unhairing. D. Burton. *J. Soc. Leather Trades' Chemists*, **42**, 403–14 (1958).—The structure and growth of hair and epidermis are discussed, after which suggestions are given for experimenters examining the efficiency of various unhairing agencies. Proposed methods for loosening hair and opening fiber structure are reviewed. The action of low temperature, warm water, bacteria, enzymes, and alkaline solutions with and without reducing or oxidizing agents, is discussed. J.M.C.

Report of the Physical Testing Commission, International Union of Leather Chemists' Societies. R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **42**, 378–93 (1958).—A summary of the test procedure decisions made by the Commission at the meeting held June 25–27 in Switzerland. Recommended physical test methods of which descriptions are given include sampling, conditioning, measurement of thickness, apparent density, tensile strength, percentage elongation caused by a specific load, and percentage elongation at break. J.M.C.

Review of Applied Analysis : Coatings. M. H. Swann, M. L. Adams, and G. G. Esposito. *Anal. Chem.*, **31**, 674–78 (1959).—A review of important contributions to coating analysis from October 1956, particularly the identification and determination of different high polymers (resins, etc.). H.B.M.

Adhesion. II. Method of Measuring Shrinkage Stress in Restrained Gelatin Films. R. C. Weatherwax, B. Coleman, and H. Tarkow. *J. Polymer Sci.*, **27**, 59–66 (1958); *Chem. Abstr.*, **53**, 5818g.

Reduction of Chromium(VI) by Different Reducing Agents. M. T. Beck and I. Bardi. *Acta Univ. Szegediensis. Acta Phys. et Chem.* (N.S.), **4,** 54–58 (1958) (in English); *Chem. Abstr.*, **53,** 5941*b*.

Coordination of Carboxylic Acids with Olated Chromic Chloride. C. A. Simpson. *Univ. Microfilms* (Ann Arbor, Mich.), *L. C. Card* **No. Mic 58–5302,** 97 pp.; *Dissertation Abstr.*, **19,** 970 (1958); *Chem. Abstr.*, **53,** 5948*f*.

Collagen Content of Normal Connective Tissue, of Tissue Surrounding a Tumor, and of Growing Rat Sarcoma. M. Grabowska. *Nature*, **183,** 1186–87 (1959).—In the first stage of development of a tumor there is a rapid decrease in the collagen content, after which the level remains unchanged. The collagen level in normal tissue is higher than that of tissue surrounding the tumor. This suggests that the subcutaneous tissue reacts to the tumor either by decreased synthesis or by increased catabolism of collagen. C.L.D.

A Second-Order Transition Temperature in Wool Fibers in the Post-Yield Region. M. Feughelman, A. Haly, and B. Rigby. *Textile Research J.*, **29,** 311–13 (1959).—A second-order transition temperature, indicated by a change in certain physical properties, exists for stretched wool fibers in water for the range 60°–70°C. At all lower temperatures studied, a fiber under a constant rate of loading passes from yield to post-yield regions at about 30% extension. At temperatures above 60°–70°C. the extension at the change from yield to post-yield region increases with increase of temperature. Chemically and physically modified wool fibers have transition temperatures which differ from that of the unmodified fiber. C.L.D.

Chemistry of Condensed Tannins. J. Seakins. *Nature*, **183,** 1168–69 (1959).—A review is given of papers presented at a meeting of the Plant Phenolics Group at the University of London (Jan. 6, 1959). The authors and titles are: "Acid-catalyzed Polymerization of Phenolic Compounds" by B. Brown; "Oxidative Polymerization Mechanisms for Catechins" by D. Hathway; "Oxidative Condensation in Tea Fermentation" by E. Roberts; "Methods for the Investigation of Complex Leucoanthocyanins" by T. Swain; "Formation of Condensed Tannins in Plants" by W. Hillis; and "Flavans of the Resorcinol Series in Relation to the Chemistry of Commercially Important Condensed Tannins" by D. Roux. C.L.D.

The Supercontraction of Wool Fibers by Aromatic Compounds. W. Crewther. *J. Soc. Dyers Colourists*, **75,** 189–94 (1959).—The kinetics of supercontraction of wool fibers have been investigated with solutions of phenol and other aromatic compounds over a wide range of concentrations and pH. The phenolate ion is more effective than un-ionized phenol in causing supercontraction. It is suggested that the two forms of phenol cause contraction by different mechanisms. The conclusion that sodium phenolate is chiefly responsible for the contraction of wool fibers in alkaline phenol solutions relates this work closely with observations of the contraction of wool and collagen in solutions of salts, such as iodides. C.L.D.

Biosynthesis and Constitution of Lignin. K. Freudenberg. *Nature*, **183**, 1152–55 (1959).—A lecture which was a survey of recent work on lignin is reprinted. The biosynthesis of lignin by the method of introducing radioactive phenylalanine or D-coniferin into spruce saplings was studied. Lignin was also prepared *in vitro* from enzymatic oxidation of coniferyl alcohol; a large number of intermediates in the process have been identified by paper chromatography. Many other facts also support Freudenberg's theory that coniferin is an intermediate in the *in vivo* process and is hydrolyzed in the newly formed cells by the action of a β-glucosidase into glucose and coniferyl alcohol, the latter compound on contact with laccase and peroxidase being converted into lignin. C.L.D.

The Reaction of Wool with Sodium Hydroxide in Concentrated Salt Solutions. J. McPhee. *Textile Research J.*, **29**, 303–10 (1959).—The effect on the alkaline degradation of wool of the addition of a number of salts to 1.25*N* NaOH was studied. The swelling of wool in the alkali was decreased by some salts but was unaffected by others. The rate of sorption of OH^- was not changed by the addition of the salts. Water was sorbed preferentially from some salt solutions, but no specific anion sorption occurred. Results of practical interest are that wool can be shrinkproofed without damage by treatment with aqueous NaOH solutions containing certain salts, and that yellowing of wool in alkali can be prevented by the addition of reducing agents. The salt effect may be due to the alkaline degradation products being less soluble in the salt-alkali solutions, coupled with a low rate of diffusion of the degradation products out of the fibers which are prevented from swelling. C.L.D.

Stress-Relaxation and Permanent Set in Keratin Fibers. M. Feughelman and T. Mitchell. *Textile Research J.*, **29**, 404–9 (1959).—When a wool fiber is stretched 40% in distilled water above 60°–70°C., the bonds opposing the extension are broken; some re-form in equilibrium with the new stretched length. If the fiber is now released in water for an hour at the same temperature, the fiber retracts in length until there is a balance (when the "set" length is reached) between the elastomeric force and the re-formed bonds, which become strained during the retraction and are unbroken. Chemical treatments that retard the permanent setting of fibers appear to prevent the total rupture of all bonds strained in the original extension. These bonds assist in retracting the fiber to its original "unset" length. C.L.D.

Relationship between Structure and Technical Characteristics of Anionic Dyes. I. Mustea. *Ind. Usoara* (Bucharest), **5**, 207–10 (1958); abstr. in *J. Soc. Dyers Colourists*, **75**, 235 (1959).—Otto's theory that penetration of dyes into leather is increased by an increase of conjugated double bonds is confirmed. C.L.D.

Thermodynamics of Adsorption of Small Molecules by Proteins. S. Harrold and B. Pethica. *Trans. Faraday Soc.*, **54**, 1876–84 (1958); abstr. in *J. Soc. Dyers Colourists*, **75**, 232 (1959).—An analysis of the binding of small molecules to proteins in solution is given by the methods of adsorption thermodynamics. Physical adsorption appears to be responsible for binding. Data are given for the binding of sodium dodecyl sulfate to keratin. C.L.D.

Colour Index. Additions and Amendments. No. 3. *Am. Dyestuff Reptr.*, **48**, No. 9, 46–55 (1959). C.L.D.

The Action of Copper Ammines on Wool. C. Whewell, J. Ashworth, V. Srinivassan, and A. Vassiliadis. *Textile Research J.*, **29**, 386–93 (1959).—When wool is immersed in solutions of copper ammines, copper is absorbed, and the fibers contract. It is possible that the copper of the wool-copper complex is associated with hydroxyl groups or oxygen. The physical properties of the treated fibers are discussed. C.L.D.

Durable Waterproofing of Wool with Fatty Acid–Chromium Complexes. A. Engeler and W. Schefer. *Textil-Rund.*, **13**, 643–49 (1958); abstr. in *J. Soc. Dyers Colourists*, **75**, 233 (1959). C.L.D.

Chroming of Wool. G. Gianola, O. Meyer, and A. Lantz. *Bull. Inst. Text. France*, **(76)**, 59–70 (Aug., 1958); abstr. in *J. Soc. Dyers Colourists*, **75**, 231 (1959).—The free amino acids cystine, cysteine, tyrosine, tryptophan, methionine, serine, and histidine reduce $K_2Cr_2O_7$ in acid solution. Other common amino acids do not. Chromed wool has a reduced tyrosine (10%), tryptophan (46%), and methionine (38%) content, but total S and cystine are not reduced. The decreased solubility of chromed wool in urea-bisulfite solution indicates the formation of interchain crosslinks. Dinitrophenylation of chromed wool reduces the rate of extraction of tervalent chromium by H_2SO_4 and oxalic acid; this is taken as evidence that the amino groups of wool are involved in the crosslinks formed on chroming. C.L.D.

Improved Preservation of Tendon for Electron Microscopy through Wet Freeze-drying. D. Scott and M. Nylen. *Nature*, **183**, 1205–6 (1959).—When turkey tendon is treated with cold acetone and then with cold ethyl chloride and then dried in air, sections from methacrylate-embedded tendon fibers present a quite different appearance under the electron microscope from fibers fixed by the usual osmium tetroxide treatment. The collagen microfibrils are in close contact and form wide bands with a definite alignment of the 640 A. striations. The sheetlike configuration resembles that seen in reconstituted collagen and in teased native collagen fibrils. C.L.D.

A Survey of Skin Diseases of Hair Sheep in Kenya and Their Effect on the Finished Leather. H. F. Green. *J. Soc. Leather Trades' Chemists*, **43**, 85–88 (1959).—The survey is based on examination of 2250 low-grade dried sheepskins representative of consignments from different parts of Kenya. Selected specimens were examined histologically and then tanned. The principal features of each disease, including their effect on the leather, are given and illustrated by (*a*) photographs of the hair or flesh surfaces of the raw skins, (*b*) photomicrographs of sections through typical lesions, and (*c*) surface photographs after tanning. J.M.C.

Hide Improvement. M. Dempsey. *J. Soc. Leather Trades' Chemists*, **43**, 83–85 (1959).—A review of the discussions of the International Hide and Allied Trades Improvement Society which met in Brussels, September 14–17,

1958. Field campaigns against the warble fly in various countries and research into new methods and insecticides are reported. Preliminary reports on the utilization of soda-naphthalene salt in the preservation of hides and skins appear very favorable. J.M.C.

Zirconium Tannage—A Review of the Literature Relating to Zirconium Tannage. D. Williams-Wynn. *J. Soc. Leather Trades' Chemists*, **43,** 76–82 (1959).—Among factors affecting fixation and tanning of Zr salts the following are reviewed: pH and basicity, concentration, effect of salts on Zr uptake by hide, and effect of modification of collagen. Operations of dyeing and fatliquoring are discussed. Procedures for the analytical determination of Zr are reviewed. J.M.C.

The Source and State of the Hydroxylysine of Collagen. II. Failure of Free Hydroxylysine to Serve as a Source of the Hydroxylysine or Lysine of Collagen. F. Sinex, D. VanSlyke, and D. Christman. *J. Biol. Chem.*, **234,** 918–21 (1959).—After tritium-labeled hydroxylysine was administered to young rats, the slight amount of tritium found in either hydroxylysine or lysine of the skin collagen indicated no significant incorporation of free hydroxylysine into collagen. The preparation of tritium-labeled hydroxylysine is described along with the treatment of the rats and subsequent preparation and analysis of the skin collagen. The results reinforce the conclusion reached previously in experiments employing labeled lysine that hydroxylysine in the body collagen is formed by hydroxylation of the lysine during formation of the collagen. J.M.C.

Problems in Devising Fastness Tests for Leather. A. W. Landmann. *J. Soc. Leather Trades' Chemists*, **43,** 112–17 (1959).—The work of the S.L.T.C. Fastness Tests Committee is described. Criteria for a fastness test are accuracy, reproducibility, and adequate differentiation between samples of varying fastness. In light of these criteria the following methods are reviewed: Fastness to Washing and Transfer of Color in Washing; Fastness to Daylight; Fastness to Rubbing (dry and wet); Fastness to Water and Perspiration; Fastness to Organic Solvents; Fastness to Heat; Fastness to Water Spotting; Fastness to Marking Off. J.M.C.

Nomogram and Tables Relating to the pH of Alkaline Liquors. J. F. Shillito. *J. Soc. Leather Trades' Chemists*, **43,** 109–11 (1959).—Tables are published showing temperature correction factors for pH in the range 10°C. to 30°C. and the conversion of pH at 20°C. to hydroxyl ion activity in the range pH 11–12. J.M.C.

Committee for the Analysis of Alkaline Liquors (Chairman J. H. Bowes). Interim Report Jan. 1959. *J. Soc. Leather Trades' Chemists*, **43,** 102–03 (1959)—**Provisional Methods for the Analysis of Alkaline Liquors.** *Ibid*, 103 (1959)—**Provisional Method for the Determination of pH (Alkaline Liquors).** *Ibid*, 103–06 (1959)—**Provisional Method for the Determination of Sulfide.** *Ibid*, 106–07 (1959)—**Provisional Method for the Determination of Chlorides.** *Ibid*, 107–08 (1959). J.M.C.

Provisional Method for Testing Fastness of Colored Leather to Marking Off. *J. Soc. Leather Trades' Chemists*, **43,** 108–09 (1959).—A method intended for assessing the resistance of the color of leather to marking off, particularily during storage. A leather specimen is stored under heat and pressure in contact with filter paper, and the staining of the filter paper is assessed. J.M.C.

The Development of a Test for the Washfastness of Leather and the Staining of Accompanying Textile Materials. A. W. Landmann. *J. Soc. Leather Trades' Chemists*, **43,** 117–28 (1959).—The experimental work which provided a basis on which to establish the washfastness and staining tests is discussed. Stirring pieces of test leather in a beaker of wash solution for 10 sec. every 5 min. and rinsing by immersion in distilled water gave satisfactory washfastness ratings. Neither staining of filter paper dipped in test leather wash liquors nor measurement of optical density of wash liquor was satisfactory for estimating the tendency to stain textiles. An experiment was carried out to evaluate a series of factors which might cause significant variations in staining. It is suggested that the washing test and the test for transfer of color should be combined to assess fastness of leather as well as staining in one test. J.M.C.

Manufacture of Fancy Leather for Leather Goods from Chrome- and Vegetable-Tanned Splits. J. C. Deb. *Bull. Central Leather Research Inst., Madras*, **5,** 269–76 (1959).—Procedures are described in detail. H.B.M.

Utilization of Spent Tan Bark. Anon. *Tropical Science*, **1,** 19–20 (1959).—Uses include stall litter, as a soil conditioner after composting with manure, etc., and manufacturing of Dutch-process white lead. Most spent tan bark is used as fuel, and a special type of furnace is necessary for efficient combustion. Attempts to use spent tan bark for making paper and as a source of cellulose for nitration have not been economically successful. H.B.M.

Nonaqueous Titration Technique in Leather Research. V. Analysis of Sulfated Oils. D. Ramaswamy, P. V. Rajalakshmi, and Y. Nayudamma. *Bull. Central Leather Research Inst., Madras*, **5,** 255–68 (1959).—The sulfated oils used for fatliquoring usually are neutralized to pH 5 or higher, and all the acidic components (except most of the free fatty acids) are present as salts, assumed to be Na salts in the present work. The acidic components present are soap, $RCOONa$ (*A*), alkyl sulfate, $ROSO_3Na$ (*B*), alkyl sulfonate, RSO_3Na (*C*), Na_2SO_4 (*D*), and free fatty acids, $RCOOH$ (*E*). These are determined as follows: (1) Separate *A*, *B*, *C*, and *E* from *D* by extracting 5 g. sulfated oil with 40 ml. of 90% 2-propanol. Centrifuge the extract, and make to 50 ml. Titrate potentiometrically an aliquot (about 1 to 2 ml.) diluted with ethylene glycol–butanol (1:1) with 0.1*N* $HClO_4$ in dioxane. This titration gives *A*. (2) To another aliquot of the extract add 5 ml. of a saturated solution of Hg(II) acetate in glacial acetic acid, and heat to 80°C. for 1 hr. to convert the salts to acetates. Add 15 ml. of glacial acetic acid and 10 ml. acetic anhydride, and titrate with standard $HClO_4$ in dioxane. This titration gives $A + B + C$, and the sum of *B* and *C* is obtained by subtracting *A*. (3) The process described

under (2) is applied to a 0.02–0.05 g. sample of the original sulfated oil. This titration gives $A + B + C + D$, and D is obtained by subtracting $A + B + C$. (4) A 10–20 ml. aliquot of the 2-propanol extract is treated with 5–10 ml. of 0.5*N* HCl and and 5 ml. of water and evaporated nearly to dryness on the water bath. This hydrolyzes *B* without affecting *C*. The residue is taken up in ethylene glycol–acetone (3:2) and titrated potentiometrically with standard NaOH in ethylene glycol–butanol (1:1). Two points of inflection are obtained. The first corresponds to the neutralization of excess HCl; the difference between the first and the second represents the titration of the $NaHSO_4$ formed by hydrolysis of *B*. Subtracting *B* from $B + C$ gives *C*. (5) Finally *E* is determined by titrating a sample of the original oil with 0.2*N* NaOH in ethylene glycol–butanol (1:1). The methods, especially the determinations of *B* and *C*, were verified by applying them to mixtures containing known amounts of Na cetyl sulfate (*B*) and pure toluene sulfonic acid neutralized exactly with NaOH (*C*). These determinations appear to be accurate to within about 2%. Analyses of commercial fatliquors indicate that most of them contain both alkyl sulfates and sulfonates. The methods are claimed to be less time-consuming than conventional methods. H.B.M.

Changes in Tensile Strength at Splitting. G. Tóth and F. Waigand. *Bőr- és Cipőtechnika*, **7**, 104–06, (1957); *Hung. Tech. Abstr.*, **10**, 96 (1958).—The algebraic sum of the tensile strength of the layers obtained by splitting leather differs considerably from the strength of the unsplit leather. The assumed cause of this phenomenon has been proved by tests. The sum of the tensile strengths yielded by the split layers is only partly less because the knife cuts through a part of the fiber bundles. The other reason is that, when splitting leather into several layers, each layer rends at the point of its min. tensile strengths. In order to find out how tensile strength is affected by the simultaneous rending of several layers the tensile strength of unsplit leather is determined, that of the two split layers is measured separately, and that of the parted layers is established jointly. The tensile strength of unsplit leather is always higher than the total of the tensile strengths of the split individual layers. However the stress occurring when two layers are simultaneously torn is often smaller than the algebraic sum of the tensile stresses measured separately. In every case at simultaneous tearing the flesh-side layer—possessing lesser elongation—tore first, followed by the grain-side layer; the only exception occurred with defective grain.

An Apparatus for Determining the Quality of Sole Leather by Fatigue Testing. II. J. Zilles. *Bőr- és Cipőtechnika*, **7**, 77–79, (1957); *Hung. Tech. Abstr.*, **10**, 97 (1958); cf. *JALCA*, **54**, 175 (1959).—Results obtained with a fatigue-testing apparatus are given and compared with the values yielded by the conventional methods (tensile strength, tearing-out strength, nail-holding power, flexural elasticity, etc.). The new values are more suitable than those hitherto employed for determining leather quality but are not adequate for testing very lightly tanned leathers. Fatigue tests lasting 40 min. on the apparatus yield sufficient data for determining the intrinsic value of leathers. One-half of the quantity of leather ordinarily required suffices for conducting the tests.

Conductometric Titration of Very Weak Acids. F. Gaslini and L. Z. Nahum. *Anal. Chem.*, **31**, 989–92 (1959).—Weak and very weak acidic groups, particularly phenols, are determined by dissolving the sample in excess aqueous ammonia and titrating conductometrically with LiOH. Intersection angles are obtained that are as sharp as those given by strong acids in normal conductometric titrations. H.B.M.

Identification of Anionic Surface-active Agents by Infrared Absorption of the Barium Salts. J. W. Jenkins and K. O. Kellenbach. *Anal. Chem.*, **31**, 1056–59 (1959).—The Ba salts of organic sulfates and sufonates are insoluble in water and in hydrocarbon solvents. The organic sulfates are first separated from interfering inorganic anions (sulfates, phosphates) by extraction with alcohol and from fatty acids by acidification and extraction. The Ba salts are precipitated and washed free from water-soluble impurities with water and from fatty contaminants with *n*-pentane. The infrared spectrum is obtained on the dried sample of the Ba salt, and identification is based on comparison with spectra of authentic compounds. The molecular weight may be obtained by ashing the Ba salt and weighing the residue. H.B.M.

Influence of the Addition of Acids and Alkalies on the pH Value and on the Solubility of Vegetable Tannins. E. Sugano and K. Yamamoto. *Bull. Japanese Assoc. Leather Technol.*, **5**, 23–31 (1959) (English summary).—Titration curves of tannins were obtained, and insolubles were determined, by centrifuging. Titration to pH 6.5 is said to be a suitable method for measuring natural acidity of a tan liquor. Insolubles of condensed tannins decrease with increasing pH values, but insolubles of hydrolyzable tannins are minimum at pH 4 to 5. The salts formed in titrating a tan liquor have more effect on the insolubles of condensed tannins than hydrolyzable tannins. Author's summary (abridged).

Studies on the Change of the Composition and of the Tanning Properties of Skin Tissue. X. The Action of Proteolytic Enzymes of the Pancreas on the Components of Unhaired Skin. R. Sasaki and Y. Sato. *Bull. Japanese Assoc. Leather Technol.*, **5**, 32–41 (1959) (English summary).—The digestion of casein, keratose, elastin, and collagen and the acceleration of deliming were studied with commercial pancreatin, trypsin, and 2 fractions of enzyme extracted from pancreas. Proteolytic enzymes accelerate deliming when little NH_4Cl is used and agitation is omitted. Decomposition products of keratin (keratose) cannot be removed from the grain completely by washing but can be removed by use of large quantities of enzyme. A certain amount of phosphorus compounds can be removed from the grain by washing, and no more can be removed by enzyme. The elastolytic action of pancreatin is not proportional to its casein-digesting power; it depends on the amount of elastase in the enzyme fraction. Digestion of collagen is not proportional to time at pH 8.0 as both collagen and elastin are digested together, but digestion of collagen is proportional to time at pH 6.9, where only collagen is digested. Digestion of collagen appears to be proportional to casein-digesting potency. When skin is digested at pH 8.0 by an enzyme that digests more elastin than collagen, more amino nitrogen is found in the acid-hydrolyzed digest. Authors' summary (abridged).

Methyl Isobutyl Ketone Extraction and Determination of Metallic Salts. II. Extraction of Chromium from Solutions Containing Hydrochloric Acid and (or) Other Acids. H. Goto and Y. Kakita. *Nippon Kagaku Zasshi*, **79**, 1520–24 (1958); *Chem. Abstr.*, **53**, 8946e.

The Iodometric Titration of Formaldehyde in Alkaline Media with Conductometric Titration. D. Ceausescu. *Acad. Rep. Populare Romine Studii Cercetari Chim.*, **8**, 291–95 (1957); *Chem. Abstr.*, **53**, 8946g.

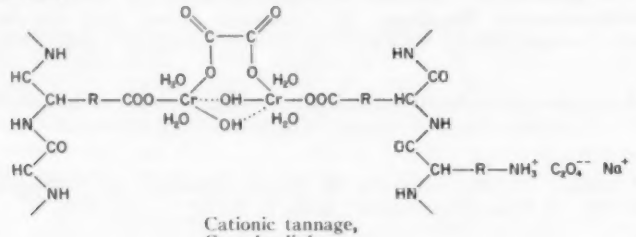
A Comparative Study of Soluble Collagenous Proteins. V. I. Mazurov and V. N. Orehkovich. *Biokhimiya*, **24**, 33–38 (1959); *Chem. Abstr.*, **53**, 9308c.

Changes in the Intensity of Cross Striation of Collagen by Imbedding of Phosphotungstic Acid. K. Kuhn, U. Hofmann, W. Grassmann, and E. Gebhardt. *Naturwissenschaften*, **45**, 521 (1958); *Chem. Abstr.*, **53**, 9321e.

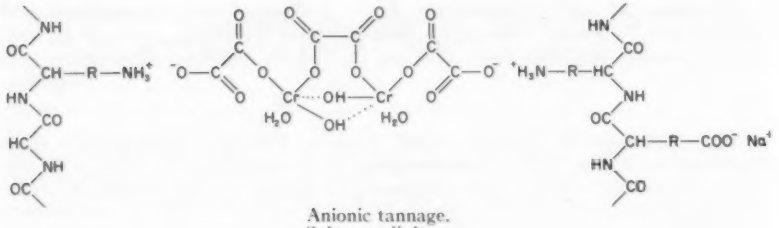
Dressing of Corrected-Grain East Indian Kips, Goatskins, and Sheepskins in Fancy Colors by Semichrome Tanning. J. C. Deb. *Bull. Central Leather Research Inst., Madras*, **5**, 319–26 (1959).—Descriptive.
H.B.M.

The Problem of Tanning with Anionic Chrome Compounds with Oxalatochromium (III) Compounds as Examples. H. Erdmann. *Das Leder*, **9**, 289–98 (1958).—The properties of dioxalato- and trioxalatochromic compounds are reviewed. Crystalline monooxalatochromic salts are not known. The trioxalato salt is resistant to alkali; only the dioxalato salt forms definite basic compounds. The basic dioxalato salt exists in trans and cis forms and the latter (cis) can aggregate, with loss of water, to form tetraoxalato-diol-dichromiate. This salt, in solution, loses 1 mol of oxalate to form trioxalato-diol-dichromiate, in which 1 oxalato group is attached, chelatelike, to 2 chromium atoms. Oxalato-chromic salts with zero basicity have practically no tanning ability. When made one-third basic they tan only when the degree of masking is so small that the chrome complex still has enough exchange groups available for tanning. There is a maximum chromium salt takeup when 2 equivalents of sodium oxalate per chromium atom are present. The tanning effect in this monooxalato range is cationic. Tetraoxalato- or trioxalato-diol-dichromi salts do not tan if tanning time is short or concentration is low, but Gustavson found a takeup of 10% Cr_2O_3 (Ts 85°C.) in a liquor having a concentration of 55% Cr_2O_3 per liter. The dioxalato salt tans very slowly; it condenses in the hide after the hide has withdrawn acid from solution. If the salt is made basic before tanning starts, it condenses to particles too large to penetrate the hide. The question of which collagen groups are united with anionic chrome complexes is often discussed but is difficult to prove because changes in the salts, such as splitting off of acid with formation of a cationic complex, must be avoided. Oxalato complexes are good for such studies because they are relatively stable. There are numerous examples in the literature of changes of anionic to cationic complexes on long aging in

aqueous solution. Trisulfatochromi complex changes on dilution to cationic, one-third basic chromic sulfate. Such a change has occurred when an anionic complex gives a true, hot-water-stable tannage. The time for this change varies: it is 30 minutes for sulfato, 3 days for sulfito, and 4 weeks for oxalato complexes. The following formulas show anionic and cationic tannages in the protein network:



Cationic tannage,
Complex linkage.
Fast to boiling.



Anionic tannage.
Salt-type linkage.
Not fast to boiling.

A true tannage of collagen can be achieved with either anionic or cationic chrome complexes. The difference is that the anionic tannages pass through a more or less stable, but not hot-water-stable, salt-type (pseudotannage) stage. If the time required for the change in the complex which leads to a true tannage is in the range of hours, then there is the advantage of greater fullness of leather and the finer grain characteristic of masked tannages. If, however, the time is too great, as with oxalate, technical use of the tannage is prohibited. In a cationic salt tannage the chrome complex is uncharged if it is combined with 2 carboxyl groups of the collagen. However, only one part of the chrome salt is attached to collagen, and the rest may have either a positive or a negative charge. If the fixed chrome complex is cationic, this charge is added to that of the amino groups of the hide. In a true anionic tannage the cationic character of the leather is considerably reduced by the presence of anionic complexes, but the cationic charge of the protein is not disturbed. A pseudo chrome tannage with anionic complexes,which block amino groups, increases the anionic character of the leather which has resulted from the negatively charged carboxyl groups. Such a leather readily takes up basic dyes or cationic chrome salts but takes up very little acid dye or vegetable tannin. I.D.C.

C-Terminal Amino Acids of the Constituent Proteins of Hides and Skins. K. Thomas Joseph and S. M. Bose. *Bull. Central Leather Research Inst., Madras,* **5,** 303–18 (1959).—The C-terminal amino acids were determined in the proteins that the authors previously analyzed for N-terminal acids (see abstract, *JALCA,* **54,** 168 [1959] by the methods used by Deasy (*JALCA,* **53,** 203 [1958]). The amounts presents were determined by Cassel's procedure (*JALCA,* **51,** 223 [1956]). The total quantities of C-terminal acids agreed fairly well with the corresponding totals of N-terminal acids, and the indicated chain lengths are said to be reasonable. The authors found glycine, alanine, valine, and leucine (or iso-leucine) as C-terminal acids in wool, collagen, citrate-soluble collagen, gelatin, elastin (*ligamentum nuchae*), reticulin (lymph node and adipose tissue), and skin globulin. Salt-soluble collagen contained no C-terminal valine. Deasy found C-terminal glycine, alanine, and leucine in collagen, but no valine. The same C-terminal acids were found in *ligamentum nuchae* (elastin) from which the collagen had been removed by autoclaving with water. Myosin, skin albumin, and skin mucoid all contained the same 4 C-terminal amino acids, but all except leucine were present in much smaller amounts than in collagen, which indicates that the C-terminal acids found in collagen cannot be ascribed to impurities. Part or all of the C-terminal glycine of wool was produced from threonine. Gelatin contained about 3 times as much C-terminal amino acid as collagen (more glycine and alanine, the same valine, less leucine) which may indicate that some peptide bonds are broken when collagen is converted to gelatin. The fact that collagen, reticulin, and elastin all have the same C-terminal acids lends support to the view that reticulin is merely a morphological variant of collagen (Küntzel, *JALCA,* **53,** 259 [1958]), and to the assertions of various workers (e.g., Burton, *Nature,* **176,** 966 [1955]) that collagen can be converted into elastin. H.B.M.

The Reaction Mechanism of Oil Tannage. S. Tanimura. *Bull. Japanese Assoc. Leather Technol.,* **5,** 10–18 (1959) (English summary).—Pieces of shark, split cowhide, and rabbit skin were tanned with unsaturated higher fatty acids, nonyl aldehyde, cod oil, and a mixture of fatty acid and a lower aldehyde. The tanning agent was either dissolved in organic solvent or emulsified. Tanning ability was judged from subjective properties of the leather produced and from increase in shrink temperature. Fatty acids and cod oil imparted the typical subjective properties of oil-tanned leather but did not raise T_s. Nonyl aldehyde had no tanning power. Acrolein had strong tanning action both on raw skin and on skin previously treated with fatty acids. The reaction mechanism of oil tannage may be a dual one. Combination tannage with HCHO and fatty acid is suggested. Author's summary (abridged).

Investigation of Synthetic Tanning Agents by Paper Chromatography. Mitio Moroi. *Bull. Japanese Assoc. Leather Technol.,* **5,** 18–22 (1959) (English summary).—Rutter's ring method of paper chromatography was applied to 4 intermediates, (sulfonation products of naphthalene, phenol, cresol, and 2-naphthol), 8 syntans made by the author, and 17 commercial syntans. The chromatograms of the condensed syntans were very similar to those of the uncondensed sulfonated products. Syntans of the same type from different manufacturers gave similar chromatograms. The spots were developed with *n*-butanol: acetic acid: water (4:1:5) and sprayed with 0.1% alcoholic diethyl-*p*-phenylene diamine. Author's summary (abridged).

Volumetric Method for Determination of Sulfates in the Presence of Chromium. R. Kling. *Chem. Anal.*, **3,** 817–20 (1958); *Chem. Abstr.*, **53,** 6906e.

The Separation of Sulfate, Sulfite, Thiosulfate, and Sulfide Ions with Anion-Exchange Resins. A. Iguchi. *Bull. Chem. Soc. Japan*, **31,** 600–5 (1958) (in English); *Chem. Abstr.*, **53,** 6906g.

Chemical Studies on Hair. V. Combination of Hair Protein with Acid (Hydrochloric Acid) and Base (Sodium Hydroxide). G. Funatsu and M. Funatsu. *Nippon Nogei-kagaku Kaishi*, **32,** 263–65 (1958); *Chem. Abstr.*, **53,** 7266h.

The Application of Antioxidants to Fish Oils to Increase Their Stability. Y. S. Davydova and V. I. Treshcheva. *Rybnoe Khozy*, **34,** No. 10, 70–74 (1958); *Chem. Abstr.*, **53,** 7630c.

Separate Determination of Nonionic Surfactants in the Presence of Ionic Agents. M. Jurata and S. Inoue. *Yukagaku*, **6,** 92–96 (1957); *Chem. Abstr.*, **53,** 7630d.

Effect of Unhairing Methods on the Properties of the Hair Obtained. M. Mycona and J Chyc-Krety. *Przeglad Skorzany*, **13,** 146–48 (1958); *Chem. Abstr.*, **53,** 7639e.

Porous Properties of Leather. II. Air Permeability of Vegetable-tanned Cowhides with Reference to their Topography. E. Raabe. *Prace Inst. Przemyslu Skorzanego*, **2,** 49–72 (1956) (English summary). **III. Heat Conductivity of Vegetable-tanned Cowhides with Reference to Their Topography.** *Ibid.*, **4,** 151–86 (1957); *Chem. Abstr.*, **53,** 7639f.

The Precipitation of Synthetic Tannins with Aromatic Amines. F. Stather and G. Reich. *Das Leder*, **10,** 1–4 (1959).—If too large a proportion of syntan is used in tanning sole leather, quality of the leather will be lowered. This is related to the fact that syntans contain high proportions of semitannins that do not make leather. The filter (hide powder) method does not distinguish between semitannins and true tannins and so is of little value for evaluation of syntans. No rapid method for evaluation is now available. Haglund (*JALCA*, **53,** 538) proposed the use of zinc or cadmium salts to precipitate true tannin, and Kilchher (*Österr. Lederzeitg.*, Festnummer 1954) used p-toluidine. Several different amines were compared, and diethylaniline was found to be most satisfactory. The diethylaniline-tannin precipitate could be removed most easily, and the excess diethylaniline acetate was completely volatile during evaporation and drying of the filtrate at 100°C. The best procedure was to treat 100 ml. of tannin solution, containing 5–10 g. per liter of dry matter, with 20 ml. of a solution containing, per liter, 37.5 g. of diethylaniline and 120 g. of acetic acid. After separating the precipitate, aliquots of the

filtrate and of the original tannin solution were evaporated and weighed, and tannin was calculated from the difference in weights. Results of analyses of several tannins by the cadmium and by the amine (diethylaniline) methods are shown in the following table:

Type of Tanning Material	Tannin Determined by		
	Filter Analysis	Cadmium Precipitation	Amine Precipitation
Pellutan EZE	24.5	19.7	18.5
Pellutan A23	45.7	31.2	31.2
Pellutan G40	33.7	24.8	22.0
Pellutan AE	24.3	19.2	21.3
Ligninsulfo acid	35.2	7.5	none
Condensed naphtholsulfo acid	25.2	14.0	cloudy
Condensed naphthalinesulfo acid	11.7	9.2	"
Pyrocatecholnovolak	27.9	16.5	"
Spruce bark	53.1	36.7	3.7
Valonia	68.1	63.7	3.0
Oak	56.8	53.3	11.2
Chestnut	63.6	60.2	18.1

Liquors from a near-practical tanning system, consisting of 8 coloring liquors and 3 layers, and run for 90 days, were analyzed by the filter, the cadmium, and the amine methods. The tannages were made with 3 syntans, a vegetable blend, and a 1:1 vegetable-syntan blend. All of the liquors gave precipitates with cadmium and in amounts that indicated tannin contents ranging from one half to one and a third times those found by the filter method. The cadmium method does not distinguish between replacement and auxiliary (semi) syntans. Amine, on the other hand, did not precipitate any of the coloring liquors except the eighth in vegetable blends and only the last two layers with Pellutan EZE and G40. These two syntans are mixed condensates of ligninsulfo acid and either dihydroxydiphenyl sulfone or technical pyrocatechol; it is not probable that the lignin fraction is condensed with the phenolic component. During tanning the phenolic component is taken up, and the lignin component accumulates in the spent liquors. All Pellutan AE liquors, both coloring and layer, gave precipitates with amine that were approximately equivalent to the tannin found by filter analysis. Pellutan AE is a mixed condensate of β-naphtholsulfo acid and phenol in which the two are condensed together; there is no component of low tanning value to accumulate in the spent liquors. Diethylaniline gives only very small precipitates with vegetable tannins and none with a water-soluble pyrocatechol-formaldehyde condensate that has decided leather-forming ability. It thus not only does not form precipitates with strongly hydrophilic tannins that are inactive tanning agents but also not with strongly tanning-active agents that are free of sulfo groups or are uncharged or only weakly charged. Surprisingly, however, these two types of tannins (true and semi) when mixed in certain proportions are precipitated almost quantitatively by diethylaniline. This fact can be used as the basis for a test for the nature of a tannin not precipitated by the amine. If a precipitate

forms on addition of condensed naphthalinsulfo acid (diethylaniline present) the solution contains a sulfo-group–free, leather-forming tannin. If a precipitate forms on addition of a pyrocatechol-formaldehyde condensate, the solution contains an excess of semitannin that is not leather-forming. This behavior explains why leather quality is not lowered unless the proportion of syntan in the tan liquors exceeds 50%. If one assumes that one sulfo group reacts with one amino group, the equivalent weight of the tannin that is precipitated can be calculated. The equivalent weight of 8 syntans ranged from 450 to 875. The equivalent weight of the tannin remaining in the liquor decreased as detanning with hide or hide powder proceeded or as salting-out progressed. Tannin by amine precipitation increased from 31.5 to 67.5 as the degree of sulfonation of the tannin decreased from 0.62 to 0.32, whereas tannin by the filter method varied irregularly between 69 and 80. I.D.C.

A New Type of Dynamic Leather-testing Machine for Determining Bending Elasticity and Bending Resistance of Sole Leather. J. Zilles. *Das Leder*, **10**, 35–37 (1959).—The test specimen is a leather disk 14.5 cm. in diameter, with the head-tail direction marked. An 8-mm. hole is punched in the center of the disk to fit over a pin in the tester. One edge of the specimen rests on a motor-driven ribbed cone. Directly above this cone is a smooth idler cone which can be loaded through a lever to put a force on the specimen approximating the weight of a person on a shoe sole. On the opposite edge of the specimen there rests a small roller mounted on a forked lever arrangement so that a known load (calculated from the formula $5d^3$, where d is the thickness of the leather in mm.) can be applied to this edge of the specimen to bend it down. A pen attached to the loading device records on a moving (1 cm/min) chart the level or droop of the edge of the specimen. After a test with a dry specimen a test on the wet specimen can be made either by dropping water on it from a flask or by filling a pan under the specimen with water. It is usually sufficient to run a test for 10 min. dry, then for 30 min. wet. After running for 10 min. (specimen speed 14 rpm) the tester is stopped with the long (head-tail) axis of the specimen in line with the loading lever arm, the load is removed, and a mark is made on the chart with the pen. Another pen mark is then made with the specimen at right angles to the first direction. Marks are made in the same manner after the wet run. A head line is made at the top of the chart with no load on the specimen, and after the run, a base line is made at the bottom of the chart with the specimen pushed down onto a quarter-sphere that is mounted on the tester under the pin that holds the specimen. Bending elasticity is calculated as percentage which the distance from base line to a given pen mark is to distance from base line to head line. Bending resistance is found by measuring the area under the curve and comparing this area with the corresponding area between the base and head lines. I.D.C.

Carbon and Oxygen Balance in the Reduction of Chrome Liquors. L. Seligsberger. *Das Leder*, **10**, 5–8 (1959).—The principal known products of the incomplete oxidation of glucose by dichromate during the manufacture of glucose-reduced chrome tan liquors are formic and oxalic acids and carbon dioxide. Other products have not been identified. To favor production of such products for study, a large excess of glucose was used, and the acid or

acid-glucose mixture was added to the dichromate (chromic acid was used in this work to avoid formation of sodium sulfate). With 1.07 mole of glucose per mole of Cr_2O_3, only 4–6% of the sugar was unaltered, but with 1.6 moles of glucose, from 43.5% to 47% was not oxidized. With 1.07 moles of glucose and reduction in an open vessel, formic and oxalic acids were formed in amounts equivalent to 19.9% and 13.1% resp. of the sugar used. With less sugar and reduction in a closed vessel the following data were obtained:

	Moles of Glucose per Mole Cr_2O_3			
	0.78		0.32	
Acid	as % of glucose	as % of available oxygen	as % of glucose	as % of available oxygen
Formic	28.2	29.2	9.8	4.1
Oxalic	12.4	19.7	14.7	9.3
Carbonic	9.2	20.0	61.6	53.4
Sum	49.8	68.9	86.1	66.8

The low amount of glucose, 0.32 mole, is only 28% more than the theoretically required amount. With 0.78 mole of glucose approximately 30% of the available oxygen had reacted with almost 50% of the glucose to form unknown oxidation products. The liquors, after oxidation, were always clear but probably contained water-soluble precursors of humic acid. The unknown oxidation products were further oxidized with cerium(IV) perchlorate which rapidly oxidizes aliphatic compounds at room temperature. Chromium was first removed from the liquor by precipitation with sodium hydroxide, glucose and oxalic acid were determined by usual methods, and volatile acids were removed by steam distillation and titrated. The remaining solution was heated for 3 hours at 45°–50°C. with 0.1*N* cerium perchlorate in 4*N* perchloric acid. Excess perchlorate was then titrated with sodium oxalate, and volatile acids were determined. The amounts of oxidized material, expressed as percentage of the glucose present in the original solutions, 0.78 and 1.07 moles resp. per mole of Cr_2O_3, were 27.4% and 18.6% if calculated from cerium perchlorate consumption, but were 44.5% and 31.3% if calculated from the amount of volatile acid. The former values were calculated using the factor of 12 for the oxidation equivalent of cerium perchlorate. This factor of 12 was reported for glucose by Smith and Duke (*Ind. Eng. Chem., Anal. Ed.*, **15**, 120 [1943]) but appears to be much too high for the decomposition products of glucose in the present work. I.D.C.

Microscopical Study and Proposed Standards of Picking Band Leathers. S. S. Guha and M. Banerjee, *J. Indian Leather Technol. Assoc.*, **7**, 47–51 (1959).—Correlation of tensile strength with microstructural characteristics showed that high tensile strength is associated with a very large amount of splitting up of fibers, low angle of weave, and high degree of compactness. There was no correlation between strength and boldness, fullness, straightness, or orderliness of the fiber pattern. A method of quality assessment based on the significant microstructural characteristics is proposed. H.B.M.

Some Problems in Chrome Tanning. I. A. Jelinek and P. H. Rao. *J. Indian Leather Technol. Assoc.*, **7**, 37–44 (1959). **II.** *Ibid.*, 65–69.—Two addresses. H.B.M.

Effect of Liming on the Tensile Strength of Picking Band Leather. A. Cakrabarty and D. Dam. *J. Indian Leather Technol. Assoc.*, **7**, 45–46 (1959). —Pieces of buffalo hide were unhaired by lime-sulfide paint (1 day), then limed for 4, 6, 8, 10, 12, 14, 16, or 18 days in saturated $Ca(OH)_2$ containing 5% NaCl. The pieces were then delimed, pickled, depickled, chrome-tanned, and dried. Increase in liming time from 4 to 18 days resulted in an increase in fixation of Cr_2O_3 from 6.1 to 10.1 g. per 100 collagen, an increase in thickness from 125% to 130% of the initial hide thickness, and a decrease in tensile strength from 68% to 55% of the strength of the raw stock. The values for the 6-day lime were nearly the same as for the 4-day lime; after 6 days the changes were nearly proportional to time of liming. H.B.M.

Comparative Tests for the Evaluation of Chrome-tanned Side Leather Limes. L. Vermes. *Bőr- és Cipőtechnika*, **8**, No. 1, 12–14, (1958); *Hung. Tech. Abstr.*, **10**, 127 (1959).—In order to produce corrected grain side leathers with a good grain, lime tests were conducted based on the fact that the quality of finished leathers is primarily determined by the lime. Argentine hides were used for the tests. It was found that leathers prepared with a lime noncorrosive to hair standing a day or two did not attain the quality of leathers treated with a one-day lime having a corrosive action to hair. However the former limes proved the most economical, producing a surface yield exceeding that of the latter limes by 3.1%. A comparison of limes corrosive to hair proves that excessive quantities of sodium sulfide (4% Na_2S by volume in 400% liquor) gave no better results than medium quantities (2% Na_2S by volume). Dilution of the lime after corrosion of the hair improved the quality of the finished leather.

The Role and the Checking of Grinding in Fiber Leather Manufacture. L. Radnóti. *Bőr- és Cipőtechnika*, **8**, No. 1, 30–33, (1958); *Hung. Tech. Abstr.*, **10**, 128 (1959).—A principal stage in fiber leather production is the grind of the fibrous raw material. Numerical values yielded by the Schopper-Riegler apparatus are not characteristic of the changes in linear dimension and of the swelling which constitute the main stages in the grinding process. The grinding process is better characterized by the virtual specific surface values computed on the basis of linear dimensions. The authors have established a numerical relationship between the degree of grinding and the linear changes in the dimensions of the fibers. This index has been denoted coefficient of grinding, $K = \frac{\Delta d\%}{\Delta l\%}$ where $\Delta d\%$ is the percentage change in the degree of grinding, $\Delta l\%$ being the percentage change in fiber length.

Natural and Synthetic Fibers. I. Description of Apparatus for Study of the Mechanical Properties of Fibers. J. F. M. Oth. *Kolloid-Z.*, **162**, 118–23 (1959). **II. Properties of Collagen Fibers. Study of Retraction of Rat Tail Tendon in the Dry State and in the Presence of Excess Water.** *Ibid.*, 124–34; *Chem. Abstr.*, **53**, 9786*b*.

Amino Acid Sequence in Proteins. H. Tuppy. *Naturwissenschaften*, **46,** 35–43 (1959); *Chem. Abstr.*, **53,** 10313*f*.

Collagen Formation by Fibroblasts of the Chick Embryo Dermis. K. R. Porter and G. D. Pappas. *J. Biophys. Biochem. Cytol.*, **5,** 153–66 (1959); *Chem. Abstr.*, **53,** 10327*f*.

Waste-Water Disposal and Treatment in the European Leather Industry. I. H. Scholz. *Rev. Tech. Ind. Cuir.*, **50,** 274–81 (1958). **II.** *Ibid.*, **51,** 13–18 (1959); *Chem. Abstr.*, **53,** 10608*c*.

Evaluation of the True Zeta-Potential of Hide and Leather Diaphragms. B. M. Ghosh and S. Ghosh. *J. Indian Chem. Soc.*, **35,** 704–8 (1958); *Chem. Abstr.*, **53,** 10818*h*.

Determination of Basicity of Iron-Organic Tanning Liquor Containing Ammonium Salts. B. Krassowski and J. Vaedtke. *Ind. Przemyslu Skorzanego*, **13,** 205–10 (1958) (English summary); *Chem. Abstr.*, **53,** 10819*e*.

Porous Properties of Leather. IV. Porosity of Vegetable-tanned Leather. E. Raabe. *Przeglad Skorzany*, **31,** 285–92 (1958) (English summary); *Chem. Abstr.*, **53,** 10820*e*.

The Sulfur Linkage in the Lignosulfonic Acid Molecule. M. N. Tsypkina, Z. V. Sevast'yanova, and M. A. Vishnyakova. *Trudy Leningrad. Lesotekh. Akad. im. S. M. Kirova*, **1956,** No. 75, 41–52; *Chem. Abstr.*, **53,** 10753*h*.

Lime Blast. C. Riess. *Das Leder*, **9,** 308–11 (1958).—Lime blast, which gives a limed hide or skin a rough, sandy feel, is caused by a crystalline deposit of calcium carbonate. The tendency of calcium carbonate to crystallize is especially great in the neutral zone. Glove leather tanners try to maintain the pH at 9 or above to prevent crystallization. Very small amounts of condensed phosphates will retard carbonate deposition (*JALCA*, **46,** 682). Calcium salts and vegetable tannins react to give dark-colored compounds that cause "lime stains" on the hide. The reaction occurs only if the calcium salt is soluble. At pH values of about 4.4 or above (the limit of solubility of calcium carbonate) only white calcium carbonate is deposited on the hide. Lime stains can be produced on filter paper and also on hide by putting a few drops of 0.5*N* calcium chloride on the paper or hide, then dipping the paper or hide into a vegetable tannin solution containing a small amount of ammonia. After a few seconds' exposure to air an intensely colored stain forms, the color and intensity of which varies with the type of tannin. Barium and strontium behave like calcium. Magnesium salts cause very faint stains, and aluminum salts none. Calcium stains are so strong that it might be thought to indicate that calcium accelerates oxidation of the tannin; this, however, is not true, as calcium retards oxidation slightly. During pretannage, formation of calcium tannate

may retard tannage so that light-colored spots form on the hide, but these spots will tan later and be dark. Coriagen, a higher molecular condensed phosphate, prevents lime stains and also greatly represses oxidation of tannin whether calcium is present or not. I.D.C.

The Behavior of Chromium Compounds during the Determination of Ash in Chrome Leather. A. Küntzel and H. Kröll. *Das Leder*, **10**, 75–8 (1959).—Ash is usually determined by heating leather at 800°C. to constant weight. Chromium compounds are then weighed as Cr_2O_3, and alkaline earth and alkali salts as oxides. The British (SLTC) method specifies heating at 600°C., adding a little water and sulfuric acid, then reheating. The weight of the sulfates so obtained is much nearer the weight of the organic metal salts originally present in the leather. Three chrome leathers with different neutral salt contents were prepared as follows: (1) tanned but not neutralized, (2) neutralized and rinsed lightly, (3) neutralized and washed until free from acid and sulfates. The ash contents (at 800°C.) of these leathers were 7.79%, 10.19%, and 3.91% resp. The ash of the last was not changed by treatment with sulfuric acid. The sulfated ash contents (at 600°) of the first 2 leathers were 14.16% and 15.35% resp. but after heating at 600° for 24 hours these values were reduced to 12.73% and 13.44%. The decreased weight was caused by loss of SO_3 from the chrome salt. The SLTC method, therefore, cannot be used. Wet oxidation with a 1:1 mixture of nitric and sulfuric acids, followed by heating at not over 400°C., was satisfactory but time-consuming. A choice must be made between (*a*) ashing at 800° and (*b*) wet oxidation and drying at 400°. Kubella (*JALCA*, **54**, 48) has proposed a factor (*f*) of 2.76 for calculating chrome tannin from Cr_2O_3 content of the leather. For the unfinished leathers used in this work *f* varied from 1.64 to 3.86 if values for ash at 800° were used and from 1.13 to 2.46 if values for ash at 400° were used. These ranges would be increased by organic tannin, fats, dyes, or finishing materials. For a given chrome leather chrome tannin is of no greater value than Cr_2O_3 content. I.D.C.

The Dechroming Action of Vegetable and Synthetic Tannins in Combination Tannages. St. Fehér and St. Kerese. *Das Leder*, **10**, 78–80 (1959).—The leaching out of chromium compounds during retannage with vegetable tannins or syntans was studied. The factors investigated were time, character of the chrome tannage, and kind and pH of the organic tannin. Pieces of limed cattlehide were pickled for 45 min. in salt and sulfuric acid, then tanned for 1 day in 40% basic ammonium chrome alum solution (0.5% Cr_2O_3) and for 2 days in 50% basic chrome solution containing 2.5% Cr_2O_3. After neutralization with 0.2% soda for 6 hr., the pieces were left on a horse for 2 days. A second set of pieces was tanned as above except that the chrome tannin was masked with 0.5 mole of sodium formate and 1 mole of sodium oxalate. Retannage was in a 2000% float containing 50 g. of tannin per l. This large float was used to obtain maximum leaching. The tan liquors were used at their natural pH and also, in a second set, after adjusting to pH 3.5. During retannage small pieces of the leather were removed and analyzed for chromium. The tannins were sulfited quebracho, oak, chestnut, sumac, valonia, gambier, Tanigan extra B, Lignotan, and Syntanol. The amount of chromium leached out was proportional to the log of time and depended

on rate of diffusion from the hide. From leathers tanned with an unmasked chrome liquor and retanned for 40 days in a liquor adjusted to pH 3.5, the order of increasing leaching was as follows: valonia, chestnut, oak, quebracho, gambier, sumac. With leather tanned with a masked chrome salt the same order was found with the exception that quebracho moved to the end of the list (greastest leaching). With all materials the effect of masking was small and could not be detected with some tannins. Masked tannages were leached more by valonia but less by Tanigan extra B. Leaching by quebracho, sumac, and Syntanol A, but not by gambier, was influenced by pH. Most of the chromium went into solution at the beginning of retannage, so that shortening the time of retannage would reduce leaching very little. I.D.C.

Studies on Enzymic Unhairing and Degreasing for Production of Leather. W. Madhavakrishna and S. M. Bose. *Bull. Central Leather Research Inst., Madras,* **5,** 351–66 (1959).—Skins of various kinds were cut into sides, and one side was unhaired by either the protease of madar or the amylase of "ragi" by methods previously published (*JALCA,* **50,** 192 [1955]; also abstracts, *JALCA,* **53,** 528 [1958]; **54,** 372 [1959]). The opposite sides were limed by conventional processes. The limed skins were delimed and bated, but the enzymized skins were not. All skins were pickled. Skins for box side and glacé kid were Cr-tanned, and skins for E.I. kip, E.I. tanned goat, and sole leather were depickled and vegetable-tanned. Analyses showed no appreciable differences, except that the sides unhaired with protease fixed less vegetable tannin than either the amylase-unhaired skins or the limed skins, in each of the 3 vegetable-tanned leathers. Results of tensile strength and lastometer tests showed no appreciable differences. Microscopic examination showed the usual lack of splitting up of fibers in enzyme-unhaired skins. The enzyme-unhaired sides differed little from controls according to subjective properties; they showed a tendency to be firmer. Attempts were made to degrease sheepskins with castor bean lipase. Preliminary tests on fats extracted from sheepskin showed that lipolytic activity was maximum at 37°C. and pH 4.8. Two sheepskins, previously unhaired with madar and ragi respectively, were handled for 1 hr. in a bath containing 9 g. lipase for 6 lb. pelt in an acetate buffer at pH 4.8 at 37°C. Fat contents were determined on the fresh skin, after unhairing, and after the lipase treatment. A third skin was subjected to the lipase treatment without unhairing. The results, given below, show that the enzyme unhairing treatment removes about as much grease as the treatment with lipase, and neither treatment removes very much.

SAMPLE	FAT (%, dry basis)		
	Before Unhairing	After Unhairing	After Lipase Treatment
No. 1 — unhaired with protease	14.3	13.0	11.9
No. 2 — unhaired with amylase	13.2	11.8	10.8
No. 3 — not unhaired	12.1	—	9.9

Fats, Oils, and Waxes for Industrial Leathers. V. R. Kishore and M. A. Ghani. *J. Indian Leather Technol. Assoc.*, **7**, 70–72 (1959).— A brief discussion. H.B.M.

Microscopic Study on Origin and Location of Tannins in Plant Bodies. M. Banerjee and G. M. Datta Banik. *J. Indian Leather Technol. Assoc.*, **7**, 77–79 (1959).—Tannins are demonstrated by staining plant sections with $FeSO_4$ (illustrated), CrO_3, or $(NH_4)_2MoO_4$. H.B.M

Manufacture of Grain Garment Leather from E. I. Sheepskins. P. S. Venkatachalam and T. S. Krishnan. *Bull. Central Leather Research Inst. Madras*, **5**, 367–70 (1959).—Procedures are given for stripping, chrome-retanning, neutralizing, dyeing and fatliquoring, retanning with basic Al sulfate, and finishing. H.B.M.

Rapid Quantitative Determination of Amino Acids by High-Temperature Paper Chromatography. J. B. Himes and L. D. Metcalfe. *Anal. Chem.*, **31**, 1192–94 (1959).—An apparatus is described for separating amino acids in protein hydrolyzates by horizontal paper chromatography with methyl ethyl ketone-propionic acid-water (15:5:6) at 60°C. in 2 hr. H.B.M.

Rapid Colorimetric Method for Determining Glyoxal. C. S. Wise, C. L. Mehltretter, and J. W. Van Cleve. *Anal. Chem.*, **31**, 1241–42 (1959).—The method depends on the formation of a blue compound by the interaction of glyoxal with dianalinoethane. To a 3-ml. aliquot of the unknown, containing about 1.2 mg. glyoxal, add 3 ml. of an alcoholic solution of 1.2-dianalinoethane dihydrochloride (1.3333 g. in 100 ml.). Add exactly 0.6 ml. of concentrated HCl from a pipet. Heat for 30 min. at 77°C. Dilute to exactly 100 ml. with 95% alcohol. Read the absorption at 550 mμ and compare with a blank made with water instead of glyoxal solution. Use a solution containing approximately the same concentration of glyoxal as reference standard. Absorption is a linear function of glyoxal content from about 0.6 to 1.8 mg. The volume of added HCl should be from 0.6 to 0.9 ml., and the time of heating should be 20 to 40 min. Formaldehyde, acetaldehyde, and monosaccharides do not interfere. H.B.M.

Setting Reduced Keratin Fibers with 1-Fluoro-2,4-dinitrobenzene. P. T. Speakman. *J. Soc. Dyers Colourists*, **75**, 252–54 (1959).—Keratin fibers, when extended, reduced, and allowed to react with 2,4-dinitrofluorobenzene under either acid or alkaline conditions at 40°C., acquire a permanent set. This effect may be due to hindered mutual movement of the protein chains by the bulky side chain of the dinitrophenyl group, or to H-bonding between NO_2 groups and ambient protein chains, or to alteration of the stability of the H-bonded protein by the dinitrophenyl group. C.L.D.

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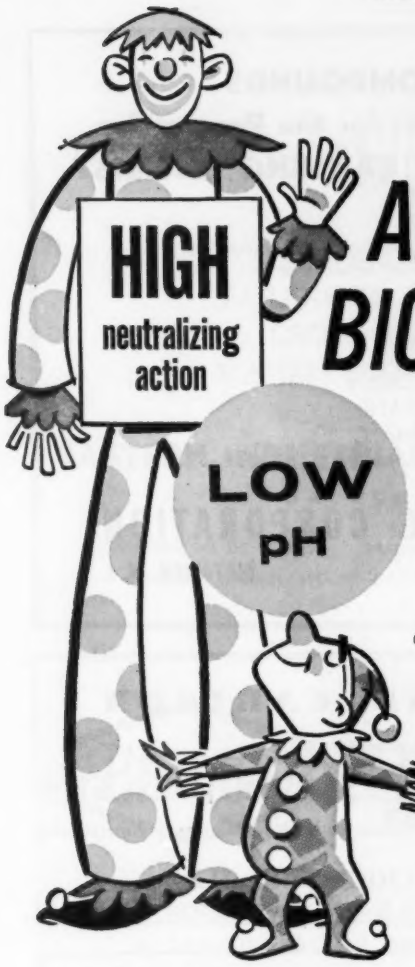

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How Tight Can You Get?

We visited a side leather tanner the other day who was wrestling with an old problem. He was trying to make a very soft straight chrome tanned side—pasted—in black and colors. As he went up percentage-wise in fatliquor using conventional sulfated oils, he finally got the softness he wanted, but by that time he had gone rag loose in the flank and belly areas of the side. The old dilemma!!

The Polarsol Approach

At this point, one of the Polarsols was introduced into the process as the fatliquor. These esterified oils seem to have the happy property of being able to produce very soft leather but, at the same time, very tight leather—a result not always obtainable with sulfated oils. Using less actual oil, this tanner now produces a butter-soft pasted side that is tight from backbone to belly.

Prove It to Yourself

Smooth, boarded and crushed softie sides for shoe upper and bag are a natural for the Polarsols. How tight can you get? Why not try the Polarsols on your pasted or toggled softie leathers and see for yourself. We'd like to send you a trial sample and complete information on how to use the Polarsols on your softie leathers. Just write or phone.

SEABOARD CHEMICALS, INC.

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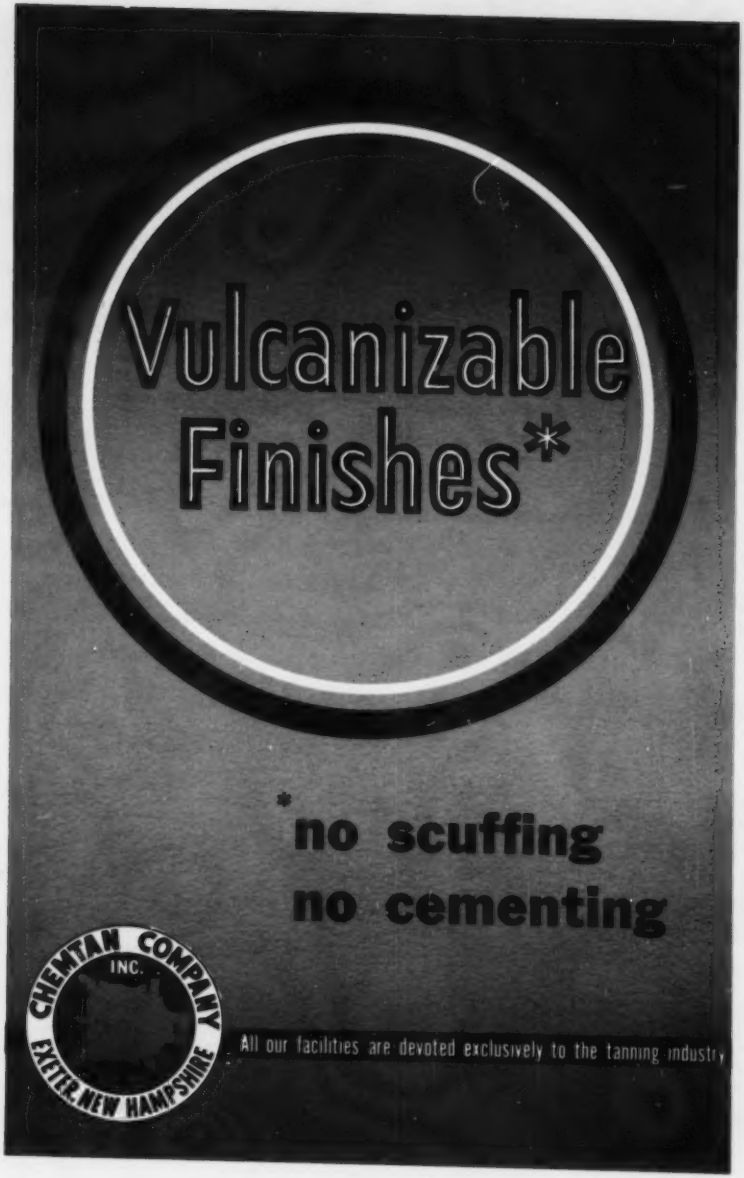
Salem, Massachusetts

In Canada: Tennant & Michaud, Ltd., Toronto and Montreal.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